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Supplementary Information

Phenanthreneimidazole derivatives as Chemosensor for Picric Acid: A First Realistic Approach

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Table S1 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $M1^+$-PA^-. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	6719(3)	4699.4(17)	4742.2(18)	33.2(5)
O2	9334(3)	4510.7(17)	5682.7(17)	30.0(5)
O3	8550(3)	1283.3(18)	6280.8(17)	35.9(6)
O4	6945(4)	-273.0(19)	4934(2)	62.8(8)
O5	4321(3)	-554.1(16)	1419.2(17)	34.4(5)
O6	4079(3)	862.8(17)	1102.5(17)	36.1(6)
O7	5727(3)	2880.9(15)	2713.3(16)	22.9(5)
N1	7772(4)	4129(2)	4985(2)	24.2(6)
N2	7546(4)	726(2)	5330(2)	31.4(6)
N3	4610(3)	463(2)	1733(2)	25.0(6)
N4	-332(3)	3712.5(19)	1671.6(19)	20.9(5)
N5	2649(3)	3942.1(18)	2533.6(19)	21.6(6)
C1	7120(4)	2931(2)	4449(2)	19.7(6)
C2	7585(4)	2420(2)	5107(2)	21.2(6)
C3	7029(4)	1282(2)	4650(2)	23.3(7)
C4	6057(4)	663(2)	3547(2)	24.4(7)
C5	5613(4)	1183(2)	2886(2)	20.9(6)
C6	6094(4)	2370(2)	3285(2)	19.1(6)
C7	924(4)	3275(2)	2142(2)	21.1(6)
C8	526(4)	2249(2)	2237(2)	21.9(6)
C9	1342(4)	2229(2)	3231(2)	25.2(7)
C10	1070(4)	1245(2)	3314(3)	27.5(7)
C11	-9(4)	285(2)	2410(3)	26.8(7)
C12	-839(4)	311(2)	1423(3)	27.2(7)
C13	-580(4)	1292(2)	1335(2)	24.3(7)
C14	619(4)	4696(2)	1764(2)	19.3(6)
C15	-77(4)	5457(2)	1387(2)	19.6(6)
C16	-1993(4)	5309(2)	825(2)	21.3(6)
C17	-2590(4)	6059(2)	465(2)	24.6(7)
C18	-1251(4)	6989(2)	681(2)	25.3(7)
C19	640(4)	7141(2)	1222(2)	21.2(6)
C20	1298(4)	6384(2)	1595(2)	19.2(6)
C21	3319(4)	6528(2)	2172(2)	19.7(6)
C22	4718(4)	7429(2)	2386(2)	24.7(7)
C23	6592(4)	7573(2)	2955(2)	28.9(7)
C24	7149(4)	6821(3)	3347(2)	29.0(7)
C25	5850(4)	5915(2)	3136(2)	25.1(7)
C26	3937(4)	5754(2)	2547(2)	20.6(6)

C27	2507(4)	4837(2)	2308(2)	19.7(6)
O8	5883(3)	2659.1(16)	665.6(17)	26.3(5)

Table S2 Anisotropic Displacement Parameters ($Å^2×10^3$) for M1$^+$-PA$^-$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O1	42.4(13)	26.4(13)	36.4(13)	15.0(11)	12.8(11)	16.4(11)
O2	32.8(12)	30.8(13)	22.1(12)	-3.5(10)	3.1(10)	11.3(10)
O3	48.2(14)	36.8(14)	22.1(12)	10.4(11)	-0.9(11)	16.1(11)
O4	126(2)	24.4(14)	30.7(14)	6.8(15)	-4.4(15)	15.9(12)
O5	53.3(14)	19.9(12)	24.0(12)	-2.5(10)	2.9(11)	8.6(10)
O6	48.4(14)	33.3(13)	24.1(12)	-3.4(11)	-6.2(11)	18.5(11)
O7	25.5(10)	25.8(11)	24.0(11)	8.6(9)	6.6(9)	16.4(10)
N1	31.3(14)	23.0(14)	20.8(14)	5.0(12)	10.5(12)	10.5(12)
N2	49.7(17)	24.1(16)	21.0(15)	10.5(13)	5.4(13)	11.0(13)
N3	28.4(13)	25.2(15)	23.1(14)	-0.3(11)	4.7(11)	14.1(12)
N4	21.5(12)	24.4(14)	20.2(13)	5.9(10)	5.0(11)	12.9(11)
N5	22.5(13)	24.7(14)	21.1(13)	6.7(11)	4.9(11)	13.4(12)
C1	18.4(14)	19.0(15)	21.7(16)	1.9(12)	6.0(13)	8.9(13)
C2	20.1(14)	25.6(17)	18.4(16)	7.2(12)	6.3(13)	9.4(14)
C3	30.8(16)	24.9(17)	18.4(16)	7.0(13)	6.9(13)	13.0(14)
C4	31.6(16)	21.0(16)	23.7(17)	7.3(13)	8.1(14)	12.1(14)
C5	21.9(14)	23.7(16)	15.6(15)	0.7(12)	1.0(12)	9.3(13)
C6	18.3(14)	23.5(16)	20.2(16)	6.7(12)	8.0(12)	12.2(14)
C7	27.2(16)	22.5(16)	15.5(15)	6.0(13)	6.7(13)	9.5(13)
C8	24.3(15)	22.3(16)	24.0(16)	5.4(13)	8.7(13)	13.7(14)
C9	27.6(16)	25.7(17)	27.2(17)	6.6(13)	8.5(14)	15.3(15)
C10	29.1(16)	33.4(19)	30.5(18)	10.9(14)	11.0(14)	21.8(16)
C11	29.6(16)	23.5(17)	34.6(19)	7.3(14)	11.0(15)	18.2(15)
C12	28.8(16)	23.3(17)	30.1(18)	5.5(13)	7.9(14)	12.3(15)
C13	27.7(16)	26.6(17)	25.6(17)	9.9(13)	9.1(14)	16.1(15)
C14	23.0(15)	18.3(15)	16.9(15)	3.3(12)	7.8(12)	7.2(13)
C15	25.1(15)	18.5(15)	15.9(15)	7.0(12)	6.9(12)	7.2(13)
C16	24.0(15)	20.7(16)	18.1(15)	4.7(13)	5.3(13)	7.6(13)
C17	25.5(16)	28.2(17)	18.9(16)	8.8(13)	3.9(13)	9.5(14)
C18	33.9(17)	24.8(17)	22.6(16)	13.5(14)	9.4(14)	13.4(14)
C19	27.9(16)	16.9(15)	19.8(16)	4.3(13)	9.0(13)	7.7(13)
C20	24.9(15)	17.9(15)	13.4(14)	4.8(12)	5.9(12)	5.1(12)
C21	24.4(15)	19.6(15)	14.5(14)	4.8(12)	6.9(12)	6.1(12)

C22	27.0(16)	21.6(16)	23.3(16)	5.9(13)	9.4(14)	6.6(14)
C23	25.9(16)	25.7(17)	27.7(18)	-2.4(13)	9.2(14)	5.4(15)
C24	21.5(15)	35.0(19)	24.7(17)	6.3(14)	3.7(14)	8.9(15)
C25	24.8(16)	28.3(17)	22.8(16)	7.9(13)	7.9(13)	10.7(14)
C26	24.3(15)	21.3(16)	15.5(15)	4.8(12)	7.9(12)	6.3(13)
C27	23.2(15)	22.0(16)	19.3(16)	7.5(12)	7.6(13)	12.8(13)
O8	31.8(11)	25.3(12)	23.6(12)	3.3(10)	4.9(10)	13.7(10)

Table S3 Bond Lengths for M1^{+}-PA^{-}.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.226(3)	C8	C13	1.392(4)
O2	N1	1.233(3)	C9	C10	1.388(4)
O3	N2	1.229(3)	C10	C11	1.390(4)
O4	N2	1.227(3)	C11	C12	1.389(4)
O5	N3	1.243(3)	C12	C13	1.387(4)
O6	N3	1.225(3)	C14	C15	1.424(4)
O7	C6	1.258(3)	C14	C27	1.373(4)
N1	C1	1.459(3)	C15	C16	1.396(4)
N2	C3	1.448(3)	C15	C20	1.421(4)
N3	C5	1.454(3)	C16	C17	1.374(4)
N4	C7	1.333(3)	C17	C18	1.404(4)
N4	C14	1.390(3)	C18	C19	1.371(4)
N5	C7	1.336(3)	C19	C20	1.407(4)
N5	C27	1.382(3)	C20	C21	1.468(4)
C1	C2	1.366(4)	C21	C22	1.402(4)
C1	C6	1.449(4)	C21	C26	1.420(4)
C2	C3	1.384(4)	C22	C23	1.374(4)
C3	C4	1.380(4)	C23	C24	1.395(4)
C4	C5	1.377(4)	C24	C25	1.366(4)
C5	C6	1.449(4)	C25	C26	1.403(4)
C7	C8	1.463(4)	C26	C27	1.421(4)
C8	C9	1.393(4)			

Table S4 Bond Angles for M1^{+}-PA^{-}.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	N1	O1	123.8(2)	C10	C9	C8	119.6(3)
C1	N1	O1	118.5(2)	C11	C10	C9	120.2(3)
C1	N1	O2	117.7(2)	C12	C11	C10	120.0(3)

O4	N2	O3	123.4(2)	C13	C12	C11	120.1(3)
C3	N2	O3	118.1(2)	C12	C13	C8	119.8(3)
C3	N2	O4	118.5(3)	C15	C14	N4	130.5(2)
O6	N3	O5	121.9(2)	C27	C14	N4	106.7(2)
C5	N3	O5	118.1(2)	C27	C14	C15	122.8(3)
C5	N3	O6	120.0(2)	C16	C15	C14	122.9(3)
C14	N4	C7	108.9(2)	C20	C15	C14	116.4(2)
C27	N5	C7	109.3(2)	C20	C15	C16	120.7(3)
C2	C1	N1	115.5(2)	C17	C16	C15	120.7(3)
C6	C1	N1	119.5(2)	C18	C17	C16	119.1(3)
C6	C1	C2	125.0(3)	C19	C18	C17	120.9(3)
C3	C2	C1	118.6(3)	C20	C19	C18	121.3(3)
C2	C3	N2	119.3(3)	C19	C20	C15	117.2(2)
C4	C3	N2	119.4(3)	C21	C20	C15	120.5(2)
C4	C3	C2	121.3(3)	C21	C20	C19	122.2(3)
C5	C4	C3	119.7(3)	C22	C21	C20	122.1(3)
C4	C5	N3	115.8(2)	C26	C21	C20	120.9(2)
C6	C5	N3	120.6(2)	C26	C21	C22	117.0(3)
C6	C5	C4	123.5(3)	C23	C22	C21	121.6(3)
C1	C6	O7	122.4(3)	C24	C23	C22	120.3(3)
C5	C6	O7	125.8(3)	C25	C24	C23	120.2(3)
C5	C6	C1	111.8(2)	C26	C25	C24	119.9(3)
N5	C7	N4	108.5(2)	C25	C26	C21	120.9(3)
C8	C7	N4	127.0(2)	C27	C26	C21	116.2(2)
C8	C7	N5	124.6(2)	C27	C26	C25	122.9(3)
C9	C8	C7	118.9(3)	C14	C27	N5	106.6(2)
C13	C8	C7	120.8(3)	C26	C27	N5	130.4(2)
C13	C8	C9	120.3(3)	C26	C27	C14	123.1(2)

Table S5 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for M1$^+$-PA$^-$.

Atom	*x*	*y*	*z*	U(eq)
H4	-1562(3)	3424.9(19)	1353.8(19)	25.1(7)
H5	3708(3)	3828.9(18)	2880.5(19)	25.9(7)
H2	8276(4)	2838(2)	5863(2)	25.4(8)
H4a	5695(4)	-118(2)	3246(2)	29.3(8)
H9	2080(4)	2885(2)	3849(2)	30.2(8)
H10	1624(4)	1228(2)	3991(3)	33.0(9)
H11	-180(4)	-389(2)	2466(3)	32.1(9)
H12	-1585(4)	-345(2)	808(3)	32.6(8)

H13	-1154(4)	1310(2)	662(2)	29.2(8)
H16	-2895(4)	4683(2)	691(2)	25.5(8)
H17	-3892(4)	5951(2)	75(2)	29.5(8)
H18	-1662(4)	7520(2)	449(2)	30.3(8)
H19	1524(4)	7770(2)	1347(2)	25.5(8)
H22	4362(4)	7953(2)	2130(2)	29.7(8)
H23	7513(4)	8188(2)	3082(2)	34.7(9)
H24	8436(4)	6940(3)	3762(2)	34.8(9)
H25	6242(4)	5395(2)	3388(2)	30.1(8)
H8a	5760(40)	2496(19)	1188(13)	39.5(7)
H8b	5690(40)	2036(9)	93(11)	39.5(7)

Table S6 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for $M3^+$-PA^-. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	8689.5(8)	4026.0(2)	2406.3(4)	29.59(16)
O8	9314(2)	4094.7(5)	3329.7(10)	29.7(4)
C38	9271(5)	4530.4(11)	1931(2)	48.1(8)
C39	10364(4)	3676.9(11)	2068(2)	44.5(7)
O1	7075(2)	3572.5(5)	7454.6(10)	36.2(4)
O2	9894(3)	3176.7(6)	6931.8(13)	49.6(5)
O3	10398(3)	2494.1(7)	7242.2(14)	54.9(6)
O4	5925(3)	1561.5(6)	8092.2(11)	40.5(4)
O5	3565(2)	1835.1(6)	8552.3(11)	37.3(4)
O6	3702(4)	3770.1(10)	7647(2)	29.8(8)
O6a	4695(8)	3831.3(15)	8459(4)	87.8(19)
O7	2755(3)	3389.8(7)	8642.4(15)	64.3(7)
N3	9440(3)	2825.5(7)	7219.1(12)	31.8(5)
N4	4985(3)	1877.3(6)	8245.1(12)	29.5(5)
N5	3890(3)	3451.8(8)	8216.8(19)	54.8(7)
C32	6663(3)	3189.3(8)	7645.9(14)	26.8(5)
C33	7709(3)	2792.9(8)	7536.4(14)	25.5(5)
C34	7164(3)	2374.0(8)	7725.1(14)	25.5(5)
C35	5571(3)	2318.0(7)	8056.9(13)	24.2(5)
C36	4525(3)	2677.0(8)	8222.2(15)	27.6(5)
C37	5063(3)	3090.2(8)	8028.7(15)	30.3(5)
N1	7252(2)	3996.4(6)	5982.7(12)	22.2(4)
N2	7861(2)	4156.6(6)	4733.8(12)	21.9(4)
C1	7147(3)	4451.3(7)	5901.0(14)	21.1(5)
C2	6669(3)	4781.1(7)	6470.3(14)	23.1(5)
C3	6181(3)	4679.6(8)	7258.7(15)	27.5(5)
C4	5656(3)	5010.4(8)	7759.5(17)	32.7(6)
C5	5588(3)	5446.5(9)	7480.0(16)	33.2(6)
C6	6067(3)	5552.7(8)	6705.4(16)	28.3(5)
C7	6645(3)	5225.6(7)	6177.9(14)	24.2(5)
C8	7160(3)	5334.7(7)	5354.6(14)	23.3(5)
C9	7252(3)	5772.4(8)	5066.4(16)	26.5(5)
C10	7742(3)	5867.7(8)	4298.1(16)	28.3(5)
C11	8186(3)	5528.2(8)	3772.2(16)	27.9(5)
C12	8128(3)	5096.7(8)	4027.1(15)	24.3(5)
C13	7614(3)	4995.7(7)	4811.1(14)	21.9(5)
C14	7543(3)	4552.6(7)	5118.1(13)	20.6(5)
C15	7682(3)	3825.9(7)	5262.5(13)	21.6(5)

C16	7976(3)	3357.7(7)	5089.4(13)	20.9(5)
C17	9470(3)	3249.1(7)	4692.1(14)	23.7(5)
C18	9901(3)	2814.6(8)	4557.0(14)	23.8(5)
C19	8863(3)	2470.6(7)	4815.4(13)	21.5(5)
C20	9302(3)	2013.5(8)	4697.8(14)	26.0(5)
C21	8265(3)	1686.3(8)	4939.0(15)	30.3(5)
C22	6681(3)	1778.1(7)	5319.2(14)	26.9(5)
C23	5591(4)	1442.3(9)	5576.3(16)	34.1(6)
C24	4052(4)	1540.7(8)	5925.5(16)	35.3(6)
C25	3538(3)	1973.4(8)	6030.2(15)	28.7(5)
C26	4589(3)	2324.0(7)	5784.7(13)	22.8(5)
C27	4111(3)	2777.2(7)	5872.2(13)	23.2(5)
C28	5158(3)	3108.6(8)	5653.5(14)	22.8(5)
C29	6824(3)	3022.5(7)	5319.4(13)	20.2(5)
C30	7293(3)	2573.3(7)	5186.7(13)	19.8(5)
C31	6183(3)	2226.0(7)	5432.7(13)	21.4(5)

Table S7 Anisotropic Displacement Parameters ($Å^2×10^3$) for M3$^+$-PA$^-$. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S1	28.6(3)	34.1(3)	27.5(3)	-1.0(3)	8.7(2)	-1.9(3)
O8	33.4(9)	32.3(9)	25.2(9)	-0.7(7)	9.7(7)	-1.5(7)
C38	46.5(19)	55(2)	43.4(19)	0.4(16)	9.2(15)	19.8(15)
C39	36.6(16)	54(2)	44.4(19)	1.6(14)	10.3(13)	-20.5(15)
O1	50.0(11)	28.0(9)	33.2(10)	-3.6(8)	15.2(8)	4.5(7)
O2	38.1(11)	47.6(12)	66.5(14)	-8.4(9)	18.9(10)	9.2(10)
O3	41.5(12)	45.6(12)	83.9(16)	11.0(10)	30.2(11)	10.3(11)
O4	48.5(11)	26.1(9)	49.0(11)	4.7(8)	13.8(9)	3.3(8)
O5	35.3(10)	34.9(10)	43.6(11)	-5.8(8)	12.0(8)	5.6(8)
O6	32.5(18)	17.2(16)	41(2)	8.5(13)	10.2(15)	21.0(15)
O6a	104(4)	41(3)	136(5)	-4(3)	78(4)	-7(3)
O7	77.2(16)	44.5(12)	84.4(17)	17.7(11)	56.5(14)	12.0(11)
N3	29.8(11)	39.1(13)	26.9(11)	-4.5(10)	5.4(9)	2.1(9)
N4	34.0(11)	27.7(11)	26.3(11)	-1.5(9)	3.0(9)	3.6(8)
N5	45.0(14)	29.7(13)	97(2)	2.3(11)	34.6(14)	7.0(13)
C32	32.0(13)	29.5(13)	18.4(12)	-3.6(10)	1.7(9)	3.2(9)
C33	24.7(12)	32.3(13)	19.7(12)	-1.5(10)	3.8(9)	2.8(10)
C34	27.3(12)	28.7(13)	19.0(12)	1.8(10)	-1.2(9)	-0.2(9)
C35	27.4(12)	24.6(12)	19.8(12)	-0.7(10)	0.7(9)	3.8(9)
C36	25.3(13)	30.3(13)	27.5(13)	-2.2(10)	5.0(10)	2.4(10)

C37	28.8(13)	26.6(13)	36.1(14)	3.5(10)	6.9(10)	2.9(10)
N1	24.1(10)	18.0(9)	25.8(10)	-0.1(8)	8.4(8)	0.7(8)
N2	23.1(10)	19.7(10)	23.9(11)	0.1(8)	6.9(8)	-0.3(8)
C1	17.3(11)	19.5(11)	27.0(12)	-1.8(9)	4.7(9)	0.2(9)
C2	19.2(11)	24.5(12)	25.9(12)	-1.9(9)	4.3(9)	-4.5(9)
C3	25.4(12)	29.5(13)	29.3(13)	-1.8(10)	9.3(10)	-3.7(10)
C4	30.4(13)	35.2(14)	34.9(15)	-3.8(11)	12.7(11)	-6.3(11)
C5	25.0(12)	35.4(14)	40.6(15)	1.0(11)	9.9(11)	-14.7(12)
C6	21.2(12)	25.2(13)	37.9(14)	-0.1(10)	2.1(10)	-5.9(11)
C7	16.1(11)	24.4(12)	31.9(13)	-1.9(9)	3.0(9)	-3.5(10)
C8	17.2(11)	21.2(11)	31.3(13)	-1.2(9)	2.6(9)	-2.8(9)
C9	21.6(12)	20.2(12)	37.4(14)	1.2(9)	3.5(10)	-3.4(10)
C10	23.2(12)	20.3(12)	40.4(15)	-0.1(10)	0.9(10)	6.1(10)
C11	22.9(12)	29.5(13)	31.5(14)	-0.9(10)	4.5(10)	6.5(10)
C12	23.8(12)	21.4(12)	27.9(13)	-0.2(9)	4.2(9)	0.4(10)
C13	15.4(10)	21.0(11)	28.5(12)	-1.1(9)	0.8(9)	0.1(9)
C14	17.8(11)	18.9(11)	25.4(12)	-1.5(9)	3.9(9)	-0.6(9)
C15	21.3(11)	20.5(11)	24.1(12)	-0.5(9)	6.7(9)	1.1(9)
C16	22.3(11)	19.7(11)	20.9(11)	1.6(9)	3.5(9)	1.2(9)
C17	22.2(11)	24.3(12)	25.5(12)	-1.2(10)	6.7(9)	-0.1(9)
C18	19.9(11)	31.1(13)	21.2(12)	2.3(10)	5.3(9)	-2.3(9)
C19	21.8(11)	23.1(11)	19.0(11)	2.1(9)	0.7(9)	0.6(9)
C20	27.4(12)	27.9(13)	23.1(12)	4.4(10)	4.7(10)	-1.5(10)
C21	38.3(14)	22.0(12)	30.4(14)	4.5(11)	4.0(11)	0.3(10)
C22	32.7(13)	23.2(12)	24.1(12)	-0.6(10)	1.4(10)	1.0(9)
C23	43.1(15)	22.5(13)	36.5(15)	-2.9(11)	5.0(12)	3.6(11)
C24	42.7(15)	27.2(13)	36.8(15)	-10.4(12)	8.6(12)	6.0(11)
C25	28.4(13)	32.6(13)	25.6(13)	-6.4(10)	5.7(10)	2.0(10)
C26	21.2(11)	28.1(12)	17.8(11)	-3.2(9)	-1.3(9)	2.3(9)
C27	19.6(11)	29.7(12)	20.7(12)	-0.0(10)	4.1(9)	0.7(9)
C28	22.2(11)	22.2(12)	23.9(12)	2.9(9)	2.5(9)	-0.6(9)
C29	21.3(11)	21.7(11)	17.2(11)	-0.5(9)	1.9(8)	-0.2(8)
C30	21.1(11)	21.5(11)	16.2(11)	1.9(9)	0.6(8)	0.8(9)
C31	23.3(11)	22.0(11)	17.9(11)	-1.4(9)	-0.8(9)	1.9(9)

Table S8 Bond Lengths for $M3^{+}$-PA^{-}.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	O8	1.5040(17)	C5	C6	1.382(4)
S1	C38	1.787(3)	C6	C7	1.410(3)
S1	C39	1.776(3)	C7	C8	1.467(3)
O1	C32	1.248(3)	C8	C9	1.407(3)
O2	N3	1.225(3)	C8	C13	1.419(3)
O3	N3	1.227(3)	C9	C10	1.368(3)
O4	N4	1.229(2)	C10	C11	1.399(3)
O5	N4	1.235(2)	C11	C12	1.370(3)
O6	O6a	1.416(7)	C12	C13	1.403(3)
O6	N5	1.322(4)	C13	C14	1.431(3)
O6a	N5	1.326(5)	C15	C16	1.465(3)
O7	N5	1.176(3)	C16	C17	1.399(3)
N3	C33	1.455(3)	C16	C29	1.411(3)
N4	C35	1.448(3)	C17	C18	1.377(3)
N5	C37	1.458(3)	C18	C19	1.394(3)
C32	C33	1.453(3)	C19	C20	1.439(3)
C32	C37	1.447(3)	C19	C30	1.421(3)
C33	C34	1.377(3)	C20	C21	1.346(3)
C34	C35	1.378(3)	C21	C22	1.430(3)
C35	C36	1.383(3)	C22	C23	1.398(3)
C36	C37	1.362(3)	C22	C31	1.423(3)
N1	C1	1.383(3)	C23	C24	1.378(4)
N1	C15	1.347(3)	C24	C25	1.380(4)
N2	C14	1.383(3)	C25	C26	1.407(3)
N2	C15	1.331(3)	C26	C27	1.428(3)
C1	C2	1.432(3)	C26	C31	1.416(3)
C1	C14	1.368(3)	C27	C28	1.347(3)
C2	C3	1.402(3)	C28	C29	1.443(3)
C2	C7	1.423(3)	C29	C30	1.426(3)
C3	C4	1.376(3)	C30	C31	1.426(3)
C4	C5	1.392(4)			

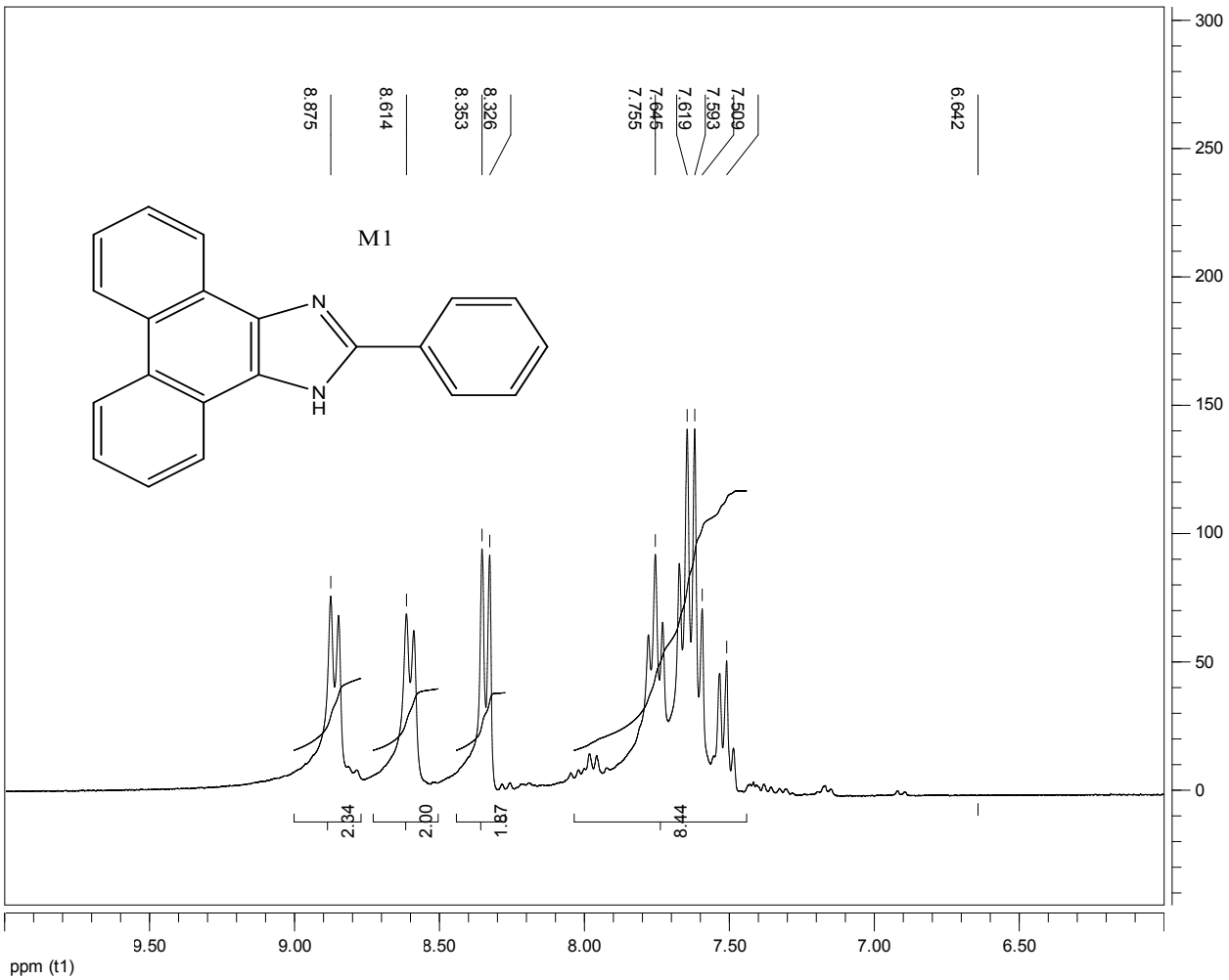
Table S9 Bond Angles for $M3^{+}$-PA^{-}.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C38	S1	O8	104.17(14)	C9	C8	C7	122.7(2)
C39	S1	O8	104.71(13)	C13	C8	C7	120.62(19)
C39	S1	C38	98.79(17)	C13	C8	C9	116.7(2)
N5	O6	O6a	57.8(2)	C10	C9	C8	121.8(2)
N5	O6a	O6	57.5(3)	C11	C10	C9	120.5(2)
O3	N3	O2	121.9(2)	C12	C11	C10	119.8(2)
C33	N3	O2	119.8(2)	C13	C12	C11	120.0(2)
C33	N3	O3	118.3(2)	C12	C13	C8	121.1(2)
O5	N4	O4	122.91(19)	C14	C13	C8	116.1(2)
C35	N4	O4	118.5(2)	C14	C13	C12	122.8(2)
C35	N4	O5	118.62(19)	C1	C14	N2	106.88(18)
O6a	N5	O6	64.6(3)	C13	C14	N2	129.7(2)
O7	N5	O6	120.4(3)	C13	C14	C1	123.4(2)
O7	N5	O6a	107.4(3)	N2	C15	N1	108.61(19)
C37	N5	O6	114.1(3)	C16	C15	N1	126.40(19)
C37	N5	O6a	116.9(3)	C16	C15	N2	124.95(19)
C37	N5	O7	120.2(2)	C17	C16	C15	117.64(19)
C33	C32	O1	125.5(2)	C29	C16	C15	122.11(19)
C37	C32	O1	122.9(2)	C29	C16	C17	120.3(2)
C37	C32	C33	111.6(2)	C18	C17	C16	121.0(2)
C32	C33	N3	120.2(2)	C19	C18	C17	120.9(2)
C34	C33	N3	116.3(2)	C20	C19	C18	122.1(2)
C34	C33	C32	123.5(2)	C30	C19	C18	119.09(19)
C35	C34	C33	119.7(2)	C30	C19	C20	118.8(2)
C34	C35	N4	119.7(2)	C21	C20	C19	121.2(2)
C36	C35	N4	119.2(2)	C22	C21	C20	121.5(2)
C36	C35	C34	121.1(2)	C23	C22	C21	122.2(2)
C37	C36	C35	119.0(2)	C31	C22	C21	119.0(2)
C32	C37	N5	119.1(2)	C31	C22	C23	118.7(2)
C36	C37	N5	115.9(2)	C24	C23	C22	121.0(2)
C36	C37	C32	125.0(2)	C25	C24	C23	121.0(2)
C15	N1	C1	108.44(18)	C26	C25	C24	120.3(2)
C15	N2	C14	109.01(19)	C27	C26	C25	122.6(2)
C2	C1	N1	130.4(2)	C31	C26	C25	119.0(2)
C14	C1	N1	107.06(18)	C31	C26	C27	118.4(2)
C14	C1	C2	122.5(2)	C28	C27	C26	121.8(2)
C3	C2	C1	123.1(2)	C29	C28	C27	121.5(2)
C7	C2	C1	116.05(19)	C28	C29	C16	123.67(19)
C7	C2	C3	120.8(2)	C30	C29	C16	118.31(19)

C4	C3	C2	120.2(2)	C30	C29	C28	117.98(19)
C5	C4	C3	120.0(2)	C29	C30	C19	120.33(19)
C6	C5	C4	120.6(2)	C31	C30	C19	119.94(19)
C7	C6	C5	121.3(2)	C31	C30	C29	119.74(19)
C6	C7	C2	117.0(2)	C26	C31	C22	119.9(2)
C8	C7	C2	121.2(2)	C30	C31	C22	119.6(2)
C8	C7	C6	121.8(2)	C30	C31	C26	120.51(19)

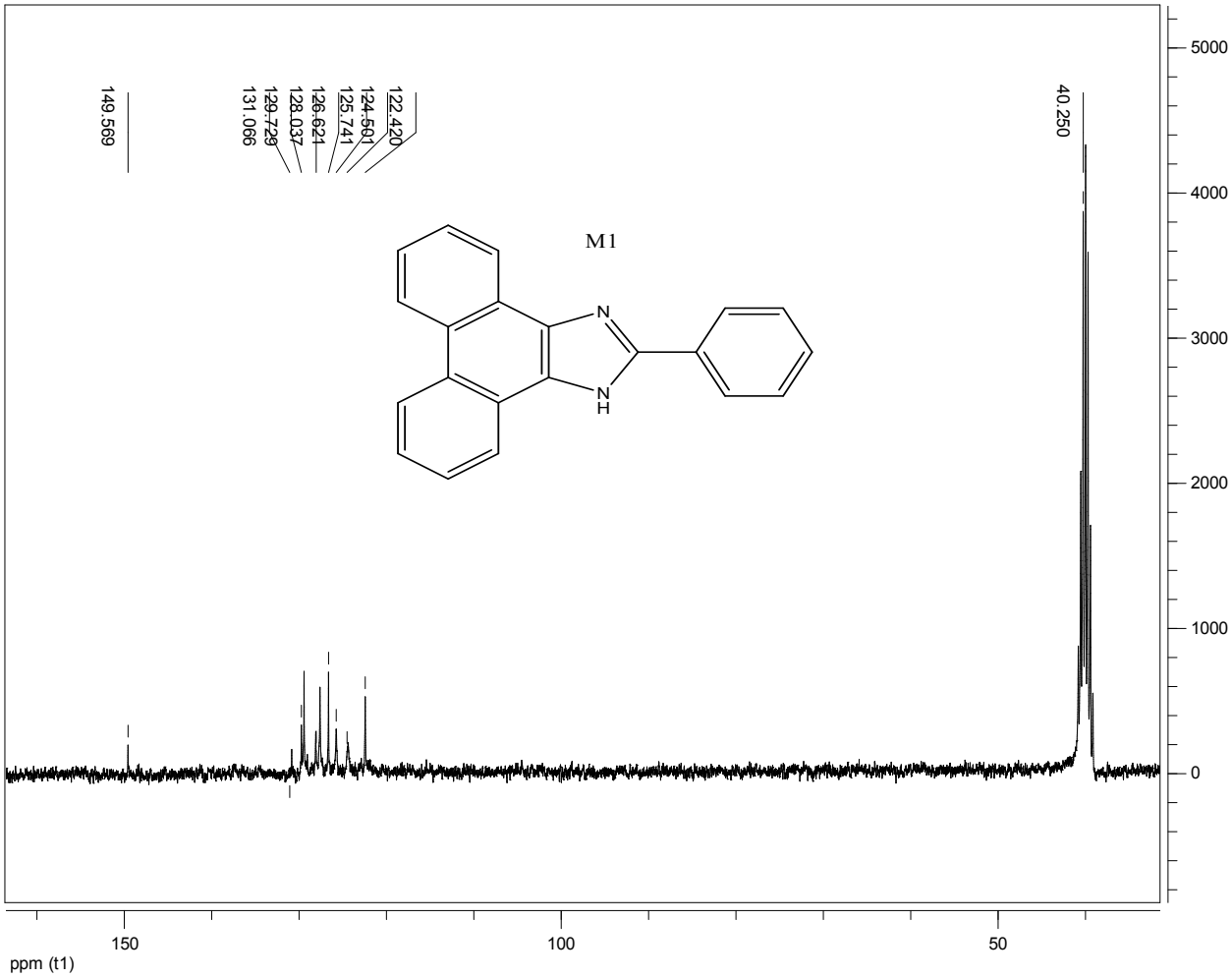
Table S10 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for M3$^+$-PA$^-$.

Atom	*X*	*y*	*z*	U(eq)
H38b	10550(40)	4598(9)	2128(18)	53(9)
H39b	10230(40)	3393(11)	2337(19)	58(10)
H39c	10090(40)	3653(10)	1480(20)	61(10)
H38a	8330(50)	4754(13)	2010(20)	92(13)
H38c	9190(40)	4456(10)	1350(20)	63(10)
H39a	11570(40)	3804(9)	2274(16)	39(7)
H34	7870(30)	2125(8)	7638(14)	25(6)
H36	3500(40)	2647(8)	8477(16)	38(7)
H1	7170(40)	3821(9)	6486(17)	44(8)
H2	8180(30)	4119(8)	4246(16)	29(7)
H3	6210(30)	4359(8)	7453(14)	30(6)
H4	5410(40)	4934(9)	8282(17)	39(7)
H5	5160(30)	5672(8)	7824(16)	36(7)
H6	6060(30)	5857(8)	6501(14)	23(6)
H9	7010(40)	6003(9)	5391(17)	41(8)
H10	7760(30)	6162(7)	4120(13)	16(5)
H11	8540(30)	5589(8)	3246(15)	28(6)
H12	8430(30)	4883(8)	3689(14)	22(6)
H17	10230(30)	3496(8)	4531(14)	23(6)
H18	10910(30)	2749(8)	4292(15)	29(6)
H20	10280(30)	1961(8)	4440(15)	30(7)
H21	8560(40)	1380(10)	4885(17)	47(8)
H24	3380(40)	1316(9)	6123(16)	41(7)
H23	5910(30)	1168(9)	5530(16)	35(7)
H25	2440(30)	2056(8)	6289(15)	30(6)
H27	3010(30)	2842(8)	6070(14)	28(6)
H28	4830(30)	3407(8)	5727(14)	24(6)



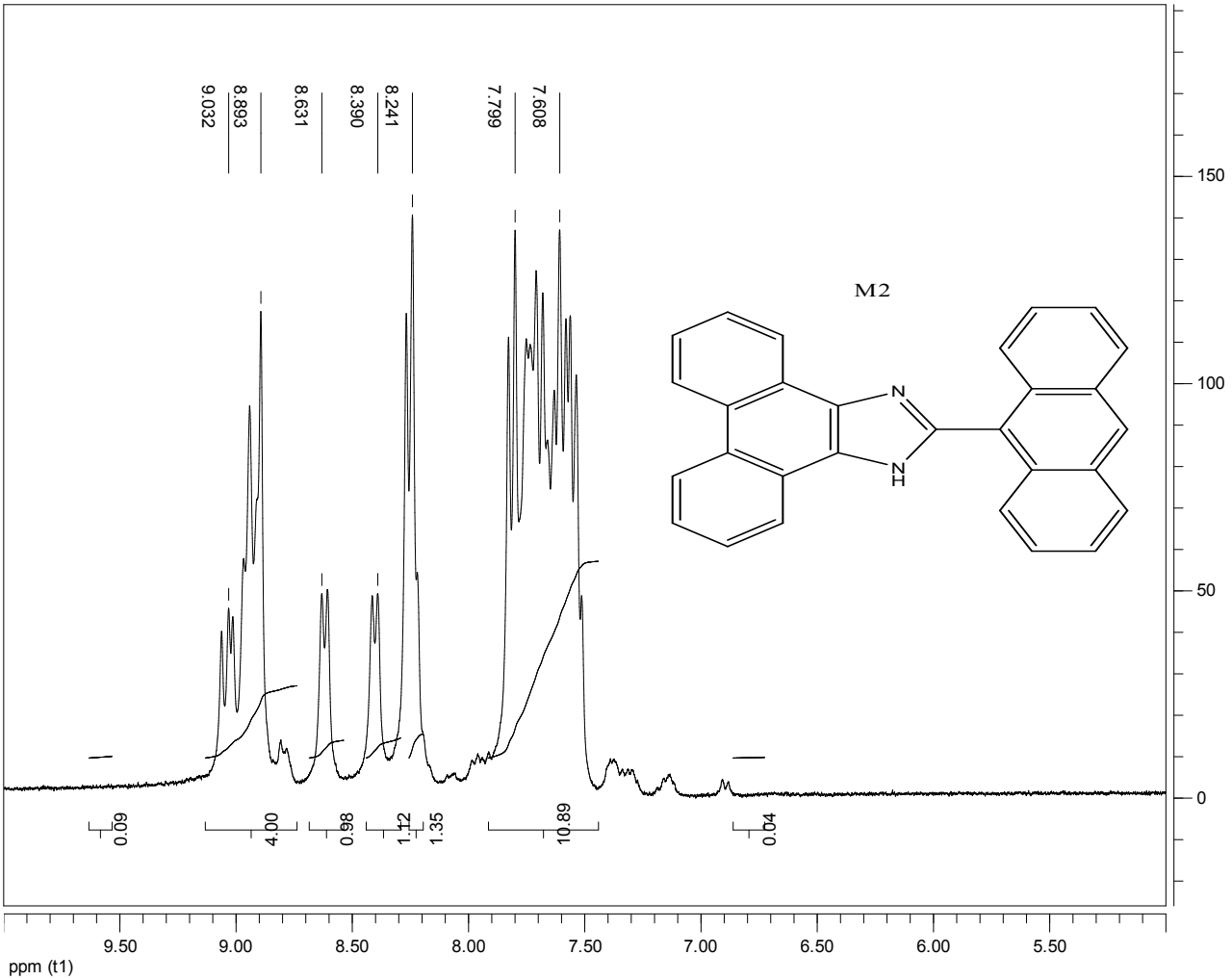
H NMR ($CDCl_3$-d_3) 300MHz δ: 8.862(d, J=8.1Hz, 2H) , 8.601(d, J=7.7Hz, 2H), 8.34(d, J=8Hz, 2H), 7.758-7.619(m, 4H), 7.509(m, 4H),

Figure S1.1H NMR spectrum of M1.



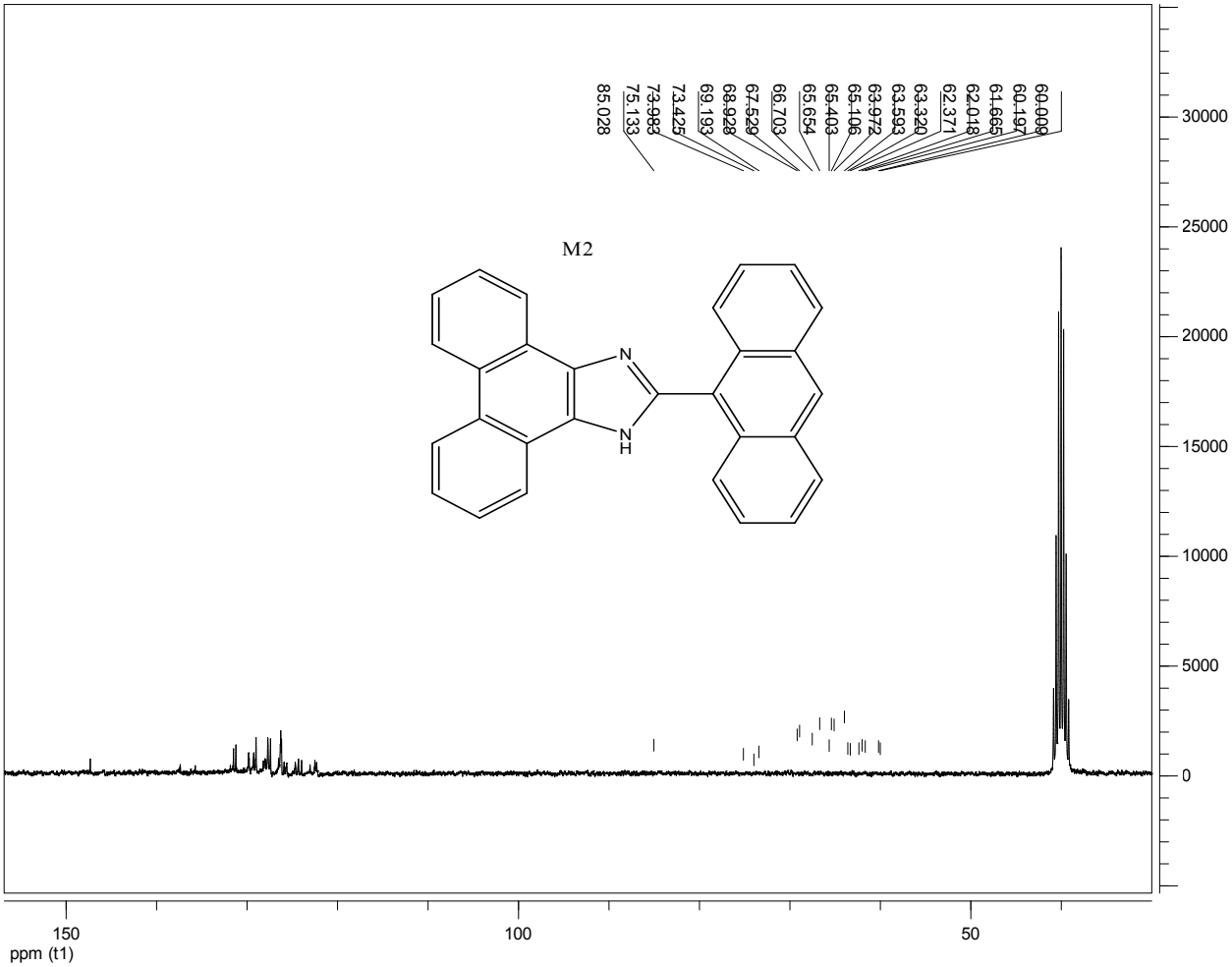
^{13}C NMR(300 MHz, $CDCl_3$) (ppm) □C: 149.588 , 131.066, 129.729 , 128.037 , 126.621 , 125.741 , 124.501 , 122.420 , 40.250

Figure S2. ^{13}C NMR spectrum of M1.



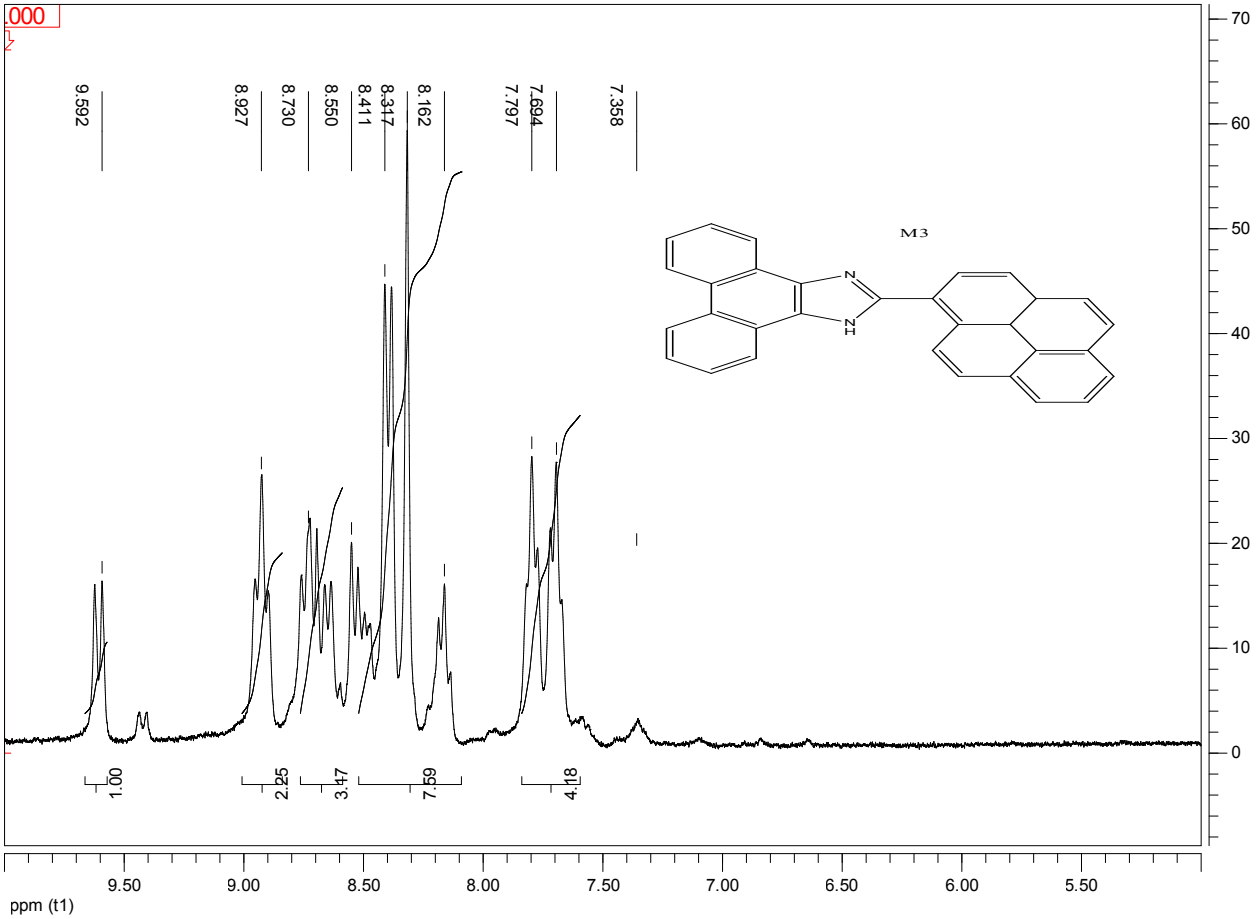
1H NMR ($CDCl_3$-d_3) 300MHz δ: 9.063(s, 1H), 9.032(d, J=5.4Hz, 1H), 8.942(m, 2H), 8.631(d, j=7.2Hz, 1H) 8.241(m, 1H), 7.799-7.514(m, 12H).

Figure S3.1H NMR spectrum of M2.



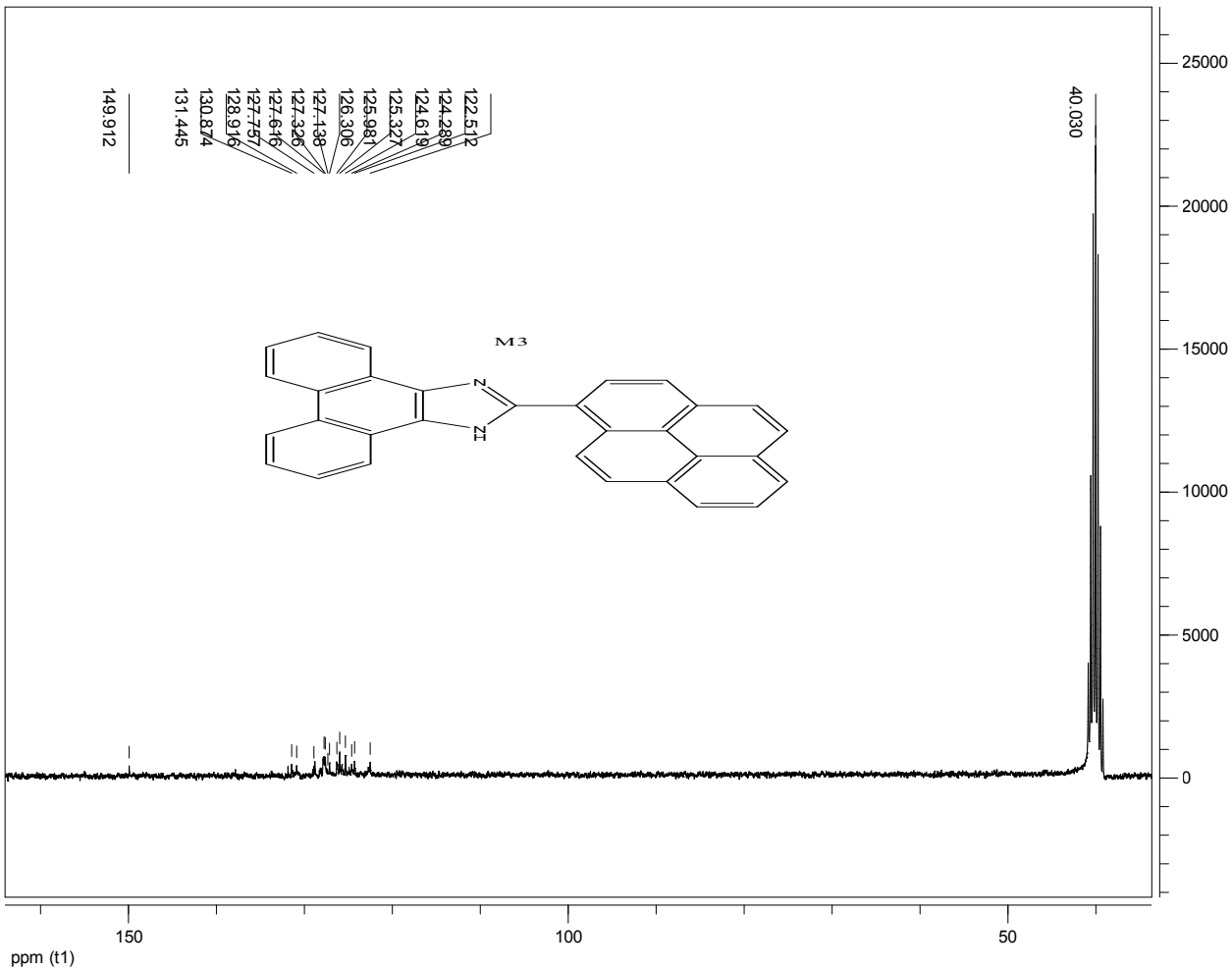
^{13}C NMR(300 MHz, $CDCl_3$) (ppm) □C: 147.329 , 137.435 , 136.284 , 135.726 , 131.495 , 131.230 , 129.831 , 129.005 , 127.956 , 127.705 , 127.407 , 126.274 , 125.895 , 125.621 , 124.672 , 124.320 , 123.967 , 122.499 , 122.310 , 40.018

Figure S4. ^{13}C NMR spectrum of M2



H NMR ($CDCl_3$-d_3) 300MHz δ: 9.608(d, J=6.0MHz, 1H), 8.927(t, J=7.8MHz, 2H), 8.695-8.636(m, 7H), 8.536(d, J=8.4MHz, 1H), 8.396(d, J=7.1MHz, 1H), 8.162(t, 2H), 7.797(t, J=6.9MHz, 2H), 7.694(t, J=7.1MHz, 2H),

Figure S5.1H NMR spectrum of M3



^{13}C NMR(300 MHz, $CDCl_3$) (ppm) □C: 149.912 , 131.445 , 130.874 , 128.916 , 127.757 , 127.616 , 127.326 , 127.138 , 126.306 , 125.981 , 125.327 , 124.819 , 124.289 , 122.512 , 40.030

Figure S6. ^{13}C NMR spectrum of M3.

FTIR of M1,M2 and M3

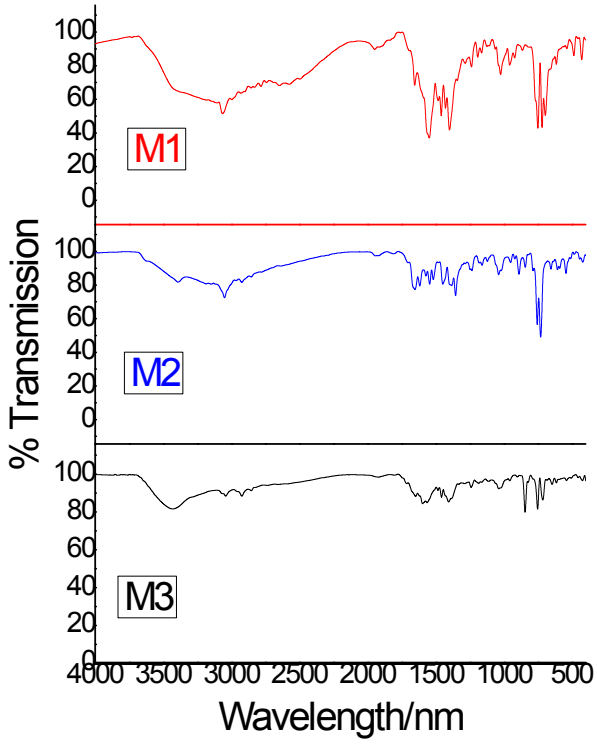


Figure S7. FTIR spectra of M1, M2 and M3.

Topology of ($M1^{+}$-PA^{-})

The analysis was performed with the ToposPro program package and the Topological Type Database (TTD) collection of periodic network topologies[1]. The nets are designated with the Topos NDn nomenclature[2], where N is a sequence of coordination numbers of all non-equivalent nodes of the net, D is periodicity of the net (D=M, C, L, T for 0-,1-,2-,3-periodic nets), and 'n' is the ordinal number of the net in the set of all non-isomorphic nets with the given ND sequence. Connectivity of the atoms in the structures was determined by means of the "Domains" method implemented in Auto CN program[3].

The structure comprises hydrogen-bonded chains consisting of 2-phenyl-3H-phenanthro[9,10-d] imidazol-1-ium cations ($M1^{+}$) connected by means of the picrate anions and water molecules. Each of the two crystallographically inequivalent $M1^{+}$ cations forms hydrogen bonds with picrate anions (PA^{-}), though only one of them is hydrogen-bonded to the water molecule (Figure S8).

The standard description[2] of a hydrogen-bonded crystal includes simplification procedure, i.e. representation of the molecular network in terms of a graph-theory approach, taking into account hydrogen bonds between molecules. The simplification procedure consists of representing the molecule by its center of mass, keeping the connectivity of the molecule with its neighbors; all intermolecular contacts between a given pair of molecules transform to the same edge between the molecular centers of mass in the simplified net (Figure. S9a). The subsequent secondary simplification of the net obtained at the previous step includes removing of the 0- and 1-coordinated nodes. Thus, this description characterizes the way molecules are hydrogen-bonded in crystal. The standard representation of the structure resulted in the underlying net of 2C1 topological type (Figure. S9b).

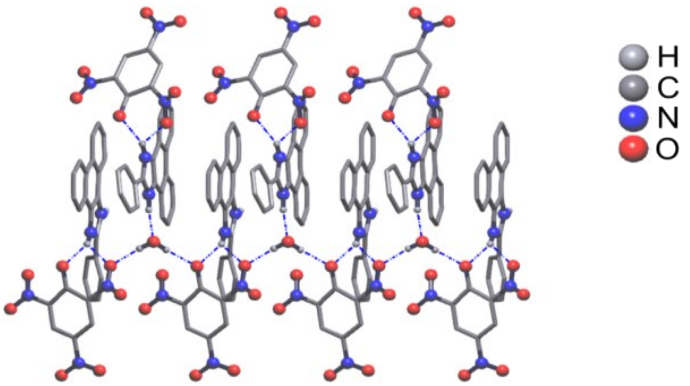


Figure S8. Fragment of the hydrogen-bonded chain running along *a* axis. Hydrogen atoms that do not participate in hydrogen-bonding are omitted for clarity.

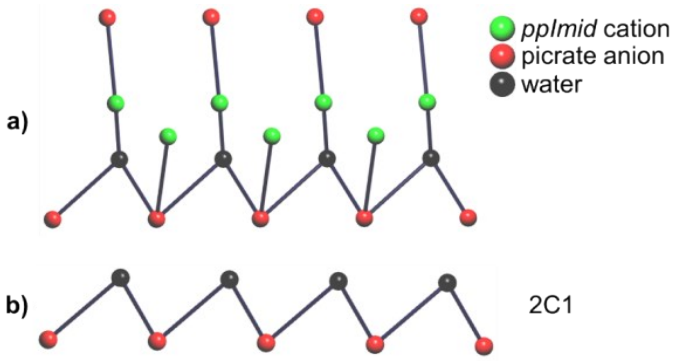


Figure S9. The standard representation of the hydrogen-bonded chain in the crystal. (a) The net obtained after primary simplification. (b) The underlying 1-periodic net of 2C1 topological type obtained after secondary simplification.

Taking into account all intermolecular contacts during the simplification procedure, one can obtain a description of the molecular packing. In the structure under investigation the hydrogen-bonded pair of $M1^+$ cations and picrate anions, presumably, is the pair of molecular ions with the highest interaction energy both due to the hydrogen bond formed and due to their opposite charge. Therefore, this pair can be considered as a building unit of the crystal. Representation of the crystal structure as a packing of the hydrogen-bonded pairs leads to the uninodal 15-c packing net with point symbol $3^{39}.4^{60}.5^6$ (Figure. S10).

In order to conduct the multilevel topological description[4] of the packing net of the hydrogen-bonded pairs ($M1^+$ cations and picrate anions) we select the value of molecular solid angle (Ωi) as a criterion, which will serve as a weight factor to be proportional to the strength of the intermolecular contact. Using the subroutine implemented in ToposPro, different subnets can be obtained from the underlying net that contains the edges of a weight no less than a specified value. Having applied the multilevel analysis, we obtain the following order of the subnets that describe the molecular packing of $M1^+$ cation and picrate anion pairs on different levels of Ωi (Table 1).

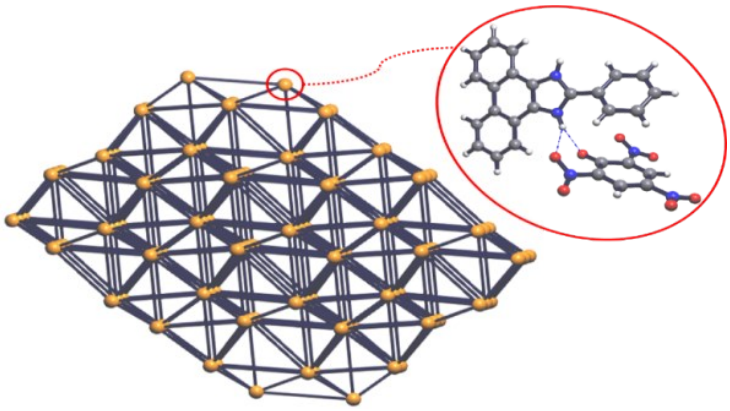


Figure S10. Underlying uninodal 15-c net of the molecular packing with unknown topological type (PS $3^{39}.4^{60}.5^{6}$).

Table 1. The subnets that describe the molecular packing on different levels of Ωi. For each of the two crystallographically inequivalent pairs, the degrees of the nodes in the net are listed. For those nets that are unknown, the point of the net is shown.

Table S11: The subnets of $M1^{+}$-PA^{-}

Node degrees	Ω_i, %	Topological type
0-c, 1-c	15.5	1M2-1
1-c, 2-c	14.5	1,2M4-1
2-c, 3-c	13.5	2,3C1
3-c, 3-c	12.5	**Hcb**
3-c, 4-c	9.0	**bbe**-3,4-Cmmm
4-c, 5-c	7.0	**stc**-4,5-C2/c
7-c, 7-c	5.0	$\{3^{4}.4^{8}.5^{6}.6^{3}\}\{3^{5}.4^{11}.5^{5}\}$
9-c, 11-c	4.0	$\{3^{15}.4^{31}.5^{9}\}\{3^{9}.4^{17}.5^{10}\}$
11-c, 11-c	3.0	$\{3^{14}.4^{30}.5^{11}\}\{3^{16}.4^{34}.5^{5}\}$
13-c, 13-c	2.0	**bcu-x**-13,13-Cmca
15-c, 15-c	1.0	$3^{39}.4^{60}.5^{6}$

Topology of ($M3^{+}$-PA^{-})

Analysis was performed with the ToposPro program package and the TTD collection of periodic network topologies[1]. The RCSR three-letter codes[5] were used to designate the network topologies. Those nets that are absent in the RCSR are designated with the Topos NDn nomenclature[2], where N is a sequence of coordination numbers of all non-equivalent nodes of the net, D is periodicity of the net (D=M, C, L, T for 0-,1-,2-,3-periodic nets), and n is the ordinal number of the net in the set of all non-isomorphic nets with the given ND sequence.

Standard simplification procedure of the hydrogen-bonded structure resulted in the 1,2M3-1 molecular packing net, with 1-, 1- and 2-coordinated nodes corresponding to picric acid anion (PA), dimethylsulfoxide (DMSO) and 2-pyrenyl-1H-phenanthro [9,10-d]imidazolium cation (M3), respectively (Figure S11). Thus, PA, DMSO and M3 form hydrogen-bonded trimers.

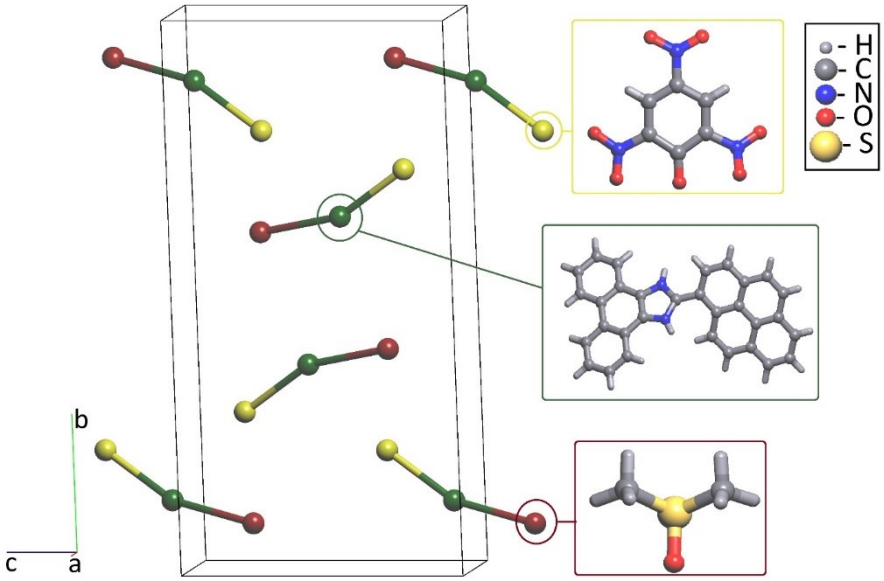


Figure S11. Underlying net of the structure. Yellow, green and red spheres correspond to PA, M3 and DMSO molecular centroids, respectively

In the packing of the hydrogen-bonded trimers, each trimer is surrounded by 14 other ones (Figure S12), forming 14T122 net.

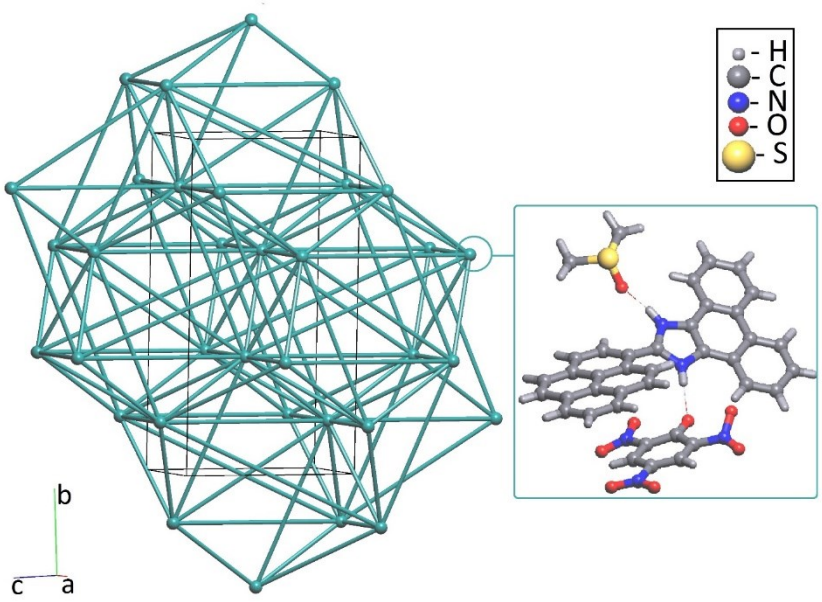


Figure S12. Underlying net of the hydrogen-bonded trimers packing. Cyan spheres correspond to the trimer centroids

Figure S10. Underlying uninodal 15-c net of the molecular packing with unknown topological type (PS $3^{39}.4^{60}.5^{6}$).

From Figure S12 it is seen, that PA anion and M3 cation are formed during proton transfer from hydroxyl of picric acid into nitrogen of 2-pyrenyl-1H-phenanthro [9,10-d]imidazole. However, hydrogen-bonded fragments form 0D net, so there is no infinite pathways for proton transport.

In order to conduct the multilevel topological description[4] of the molecular packing we select the value of molecular solid angle (Ω_i) as a criterion, which will serve as a weight factor to be proportional to the strength of the intermolecular contact. Using the subroutine Generate Representations implemented in ToposPro, different subnets can be obtained from the underlying net that contain the edges of a weight no less than a specified value (Figure S13). The 14-c molecular packing net describes the way the hydrogen-bonded trimers are assembled. Each subnet of this net contains information about the spatial arrangement of strong intermolecular contacts, assuming the Ω_i is proportional to the strength of intermolecular interaction (Table 1).

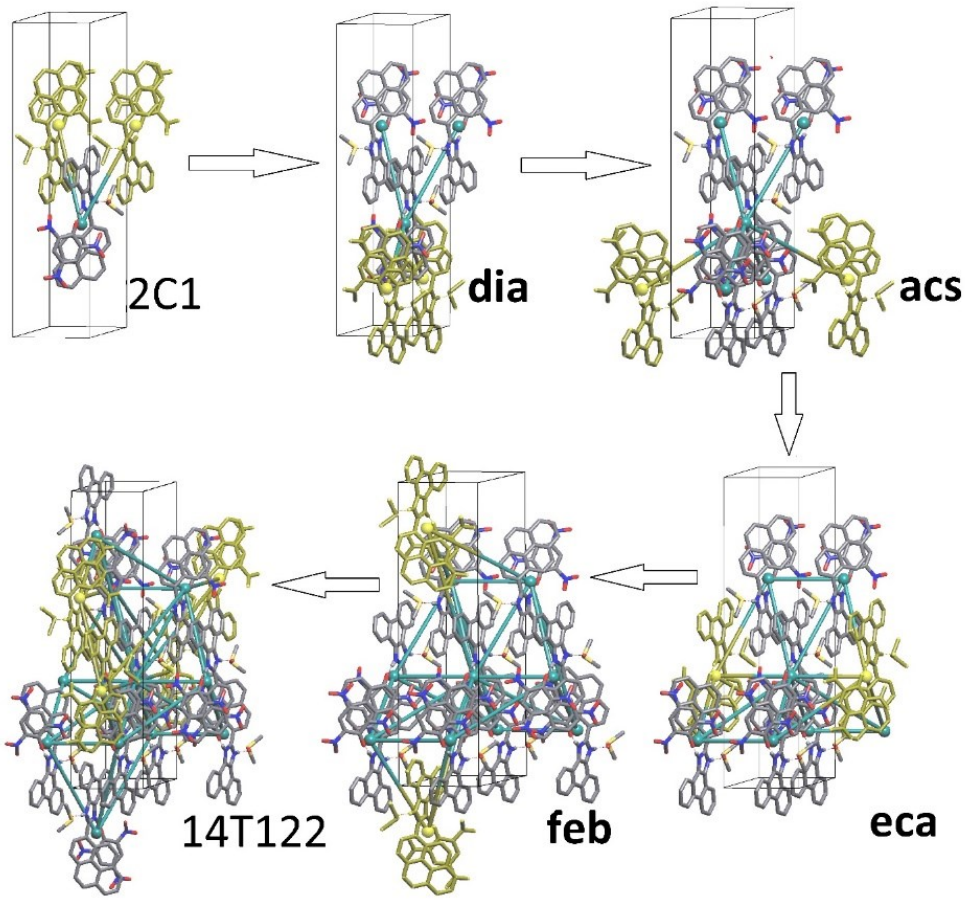


Figure S13. Subnets of the initial net corresponding to the molecular packing in structure at different levels: 2-c 2C1→ 4-c **dia** → 6-c **acs** → 8-c **eca** → 10-c **feb** → 14-c 14T122 net. Highlighted fragments correspond to the hydrogen-bonded trimers, which appear at a given Ω value.

Table S12: Values of the molecular solid angle (Ω_i) and corresponding topological types of the subnets of the molecular packing net

No. of molecules	Ω_i, %	Dimensionality	Topology
1, 2	18	1D	2C1
3, 4	12	3D	**Dia**
5, 6	8	3D	**Acs**
7, 8	6	3D	**Eca**
9, 10	3	3D	**Feb**
11-14	0	3D	14T122

Besides hydrogen bonding, π-π-interactions play important role in the structure formation. π-π-Bonds between two M3 cations appear at the value of Ω_i (13%) larger than Ω_i, corresponding to DMSO – M3 hydrogen bonding (7%), so intermolecular contacts M3 – M3 is stronger than DMSO – M3 (Figure S14). Thus, we can consider the tetramer PA – M3 – M3 – PA as building unit of the structure.

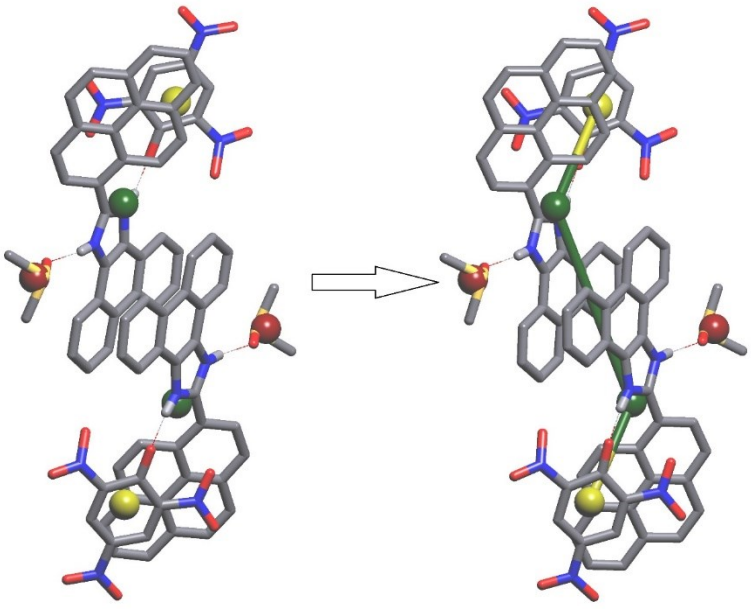


Figure S14. Molecular packing of π-π-stacked fragments. Red, green and yellow spheres correspond to DMSO, M3 and PA molecular centroids, respectively.

The tetramers form 14-coordinated net with **bcu**-x topology (Figure S15). Information about the Ω_i, dimensionality and topology of corresponding subnets is given in Table S13. Using the subroutine Generate Representations implemented in ToposPro, different subnets can be obtained from the underlying net that contain the edges of a weight no less than a specified value (Figure S16).

Table S13: Values of the molecular solid angle (Ω_i) and corresponding topological types of the subnets of the π-π-dimer packing net

No. of molecules	Ω_i, %	Dimensionality	Topology
1, 2	18	1D	2C1
3 – 6	10	3D	**Pcu**
7 – 10	4	3D	**Bct**
11 – 14	0	3D	**bcu**-x

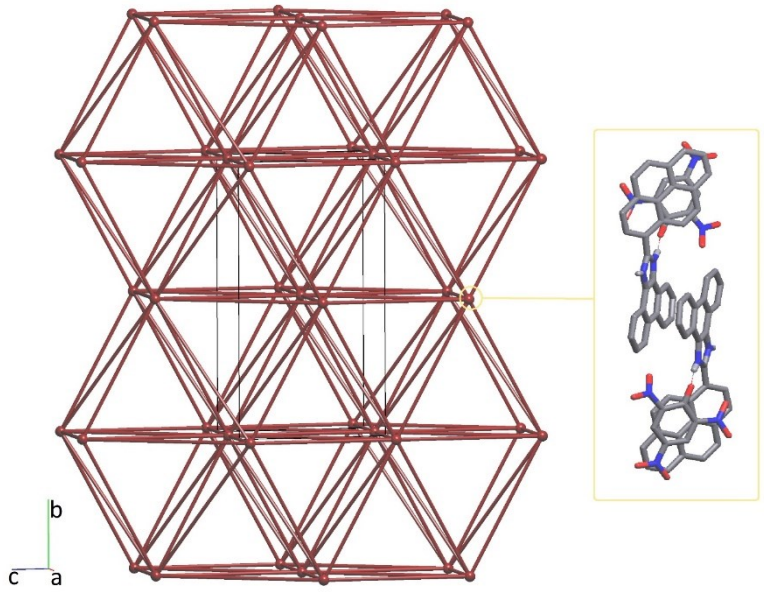


Figure S15. Underlying net of the tetramers packing. Red spheres correspond to the tetramers centroids

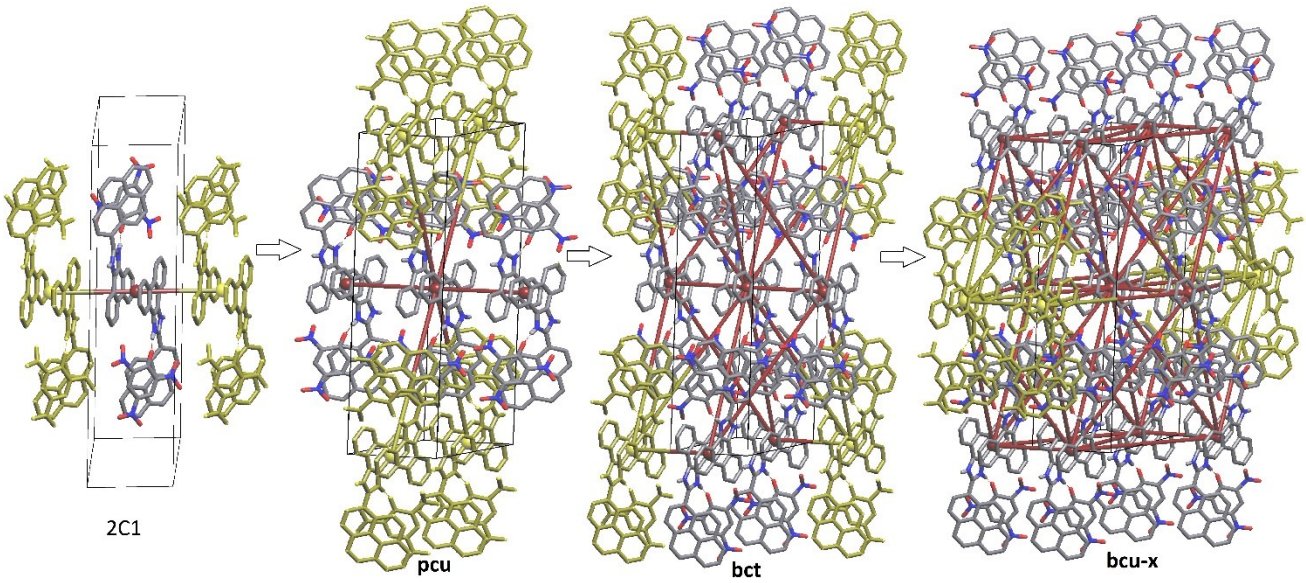


Figure S16. Subnets of the initial net corresponding to the tetramers packing in structure at different levels: 2-c 2C1→ 6-c **pcu** → 10-c **bct** → 14-c **bcu**-x net. Highlighted fragments correspond to the π-π-bonded dimers, which appear at a given Ω value.

Hirshfeld analysis of $M3^{+}$-PA^{-}

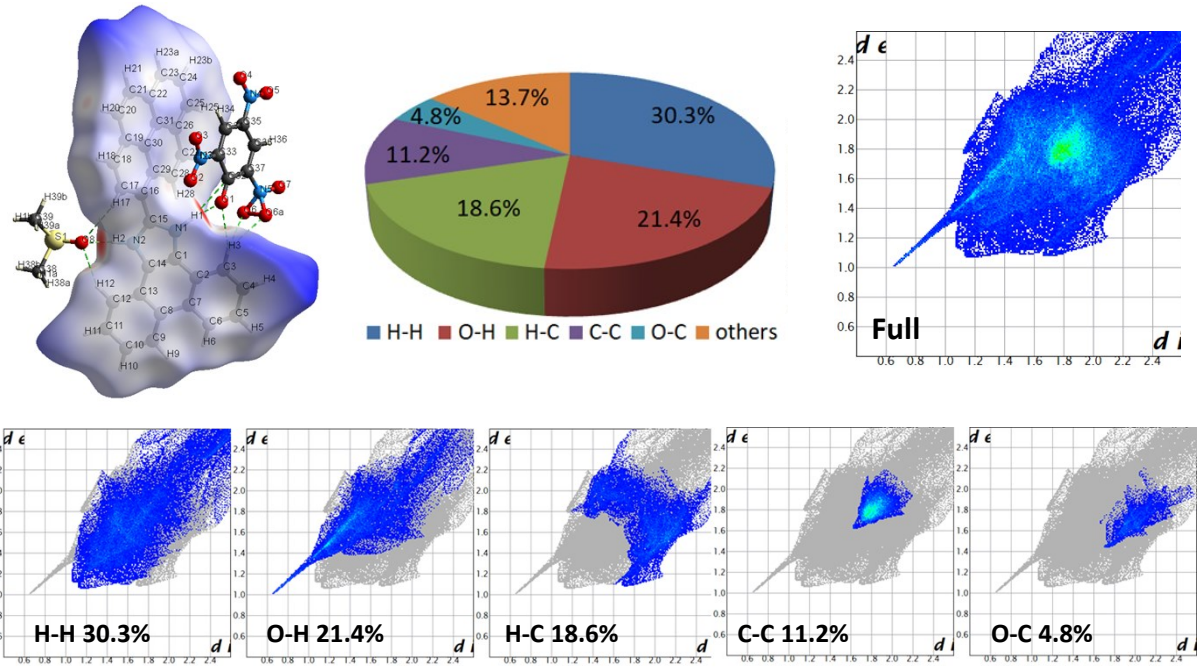


Figure S17. Hirschfeld surface for M3 with d_{norm} over the range of -.734 to 3.069. Neighboring molecules (DMSO and PA) associated with close contacts are also shown. Pie chart and FP for overall, other contacts and percentage contribution from different contacts in M3

Hirschfeld surface provides an extended qualitative and quantitative analysis of the interactions between the constituents of complex. The analysis of various interactions in $M3^{+}$-PA^{-} reveal the presence N1-H1…O1, C3-H3…O1, C3-H3…O6, C3-H3…O6a, N1-H1…C32, on one side and N2-H2…O8, C12-H12…O8, C17-H17…O8 hydrogen-bonds, on the opposite side leading to form a three-dimensional complex (Figure S17). Red spots in the Hirschfeld surface of M3 are centered at N1H1, C3H3, N2H2 and C20H20. The red spot reflecting strong electrostatic interactions are centered at N2H2. This has DMSO molecule in its vicinity, which forms electrostatic attraction between M3 unit and DMSO via N2—H2---O8. On the other side near N1H1 lies the picric acid molecule, which undergo hydrogen bonding interaction involving N1—H1---O1. The pie chart in figure S17 shows the percentage contribution of various interactions in the complex. The percentage contribution of H---H and H---O is 30.3% and 21.4% respectively. The O---H interaction includes oxygen atoms from the DMSO, nitro and phenoxide groups in PA^{-}.

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