A 2-pyridyl (py) attached phosphine imine [P(Npy)(NHpy)$_3$] and an imido phosphinate ion [P(Npy)$_2$(NHpy)$_2$]$^-$ in its Ag(I) complex

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Supporting Information

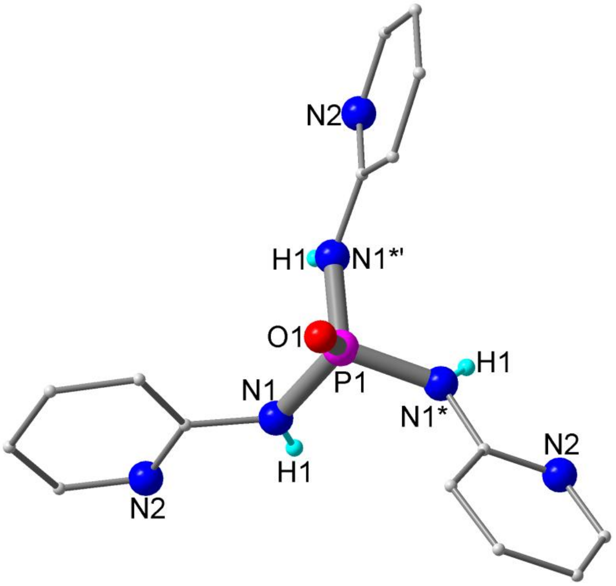
Table S1: Selected bond lengths and bond angles for compounds **2-4**

Compound	Bond lengths	Bond Angles
2	P(1)-O(1): 1.4759(17)	O(1)-P(1)-N(1)*: 113.40(4)
	P(1)-N(1)*: 1.6548(12)	O(1)-P(1)-N(1)*’: 113.40(4)
	P(1)-N(1)*’: 1.6548(12)	N(1)*-P(1)-N(1)*’: 105.27(5)
	P(1)-N(1): 1.6549(12)	O(1)-P(1)-N(1): 113.40(4)
		N(1)*-P(1)-N(1):105.27(5)
		N(1)*’-P(1)-N(1):105.27(5)
3	P(1)-N(4): 1.5737(14)	N(4)-P(1)-N(1): 102.99(7)
	P(1)-N(1): 1.6314(13)	N(4)-P(1)-N(2): 118.62(7)
	P(1)-N(2): 1.6325(14)	N(1)-P(1)-N(2): 110.15(7)
	P(1)-N(3): 1.6463(14)	N(4)-P(1)-N(3): 116.55(7)
		N(1)-P(1)-N(3): 109.47(7)
		N(2)-P(1)-N(3): 99.06(7)
4	Ag(1)-N(1) : 2.219(4)	N(1)-Ag(1)-N(42)*: 131.62(16)
	Ag(1)-N(42)*: 2.368(5)	N(1)-Ag(1)-N(2)*: 131.55(16)
	Ag(1)-N(2)*: 2.391(4)	N(42)*-Ag(1)-N(2)*:191.45(16)
	Ag(1)-Ag(2): 2.9647(7)	N(1)-Ag(1)-Ag(2): 77.65(12)
	Ag(1)-Ag(3): 3.0112(8)	N(42)*-Ag(1)-Ag(2): 149.47(13)
	Ag(1)-Ag(1)*: 3.0182(12)	N(2)*-Ag(1)-Ag(2): 67.15(11)
	Ag(2)-N(22)*: 2.191(5)	N(1)-Ag(1)-Ag(3): 70.95(12)
	Ag(2)-N(32): 2.279(5)	N(42)*-Ag(1)-Ag(3): 69.86(13)
	Ag(2)-N(2): 2.490(5)	N(2)*-Ag(1)-Ag(3): 116.52(11)
	Ag(2)-Ag(2)*: 3.1772(12)	Ag(2)-Ag(1)-Ag(3)138.52(2)
	Ag(3)-N(12)*: 2.165(5)	N(1)-Ag(1)-Ag(1)#168.30(12)
	Ag(3)-N(12): 2.166(5)	N(42)*-Ag(1)-Ag(1)*: 112.77(13)
	Ag(3)-Ag(1): 3.0113(8)	N(2)*-Ag(1)-Ag(1)*: 75.55(12)
	P(1)-N(1): 1.598(5)	Ag(2)-Ag(1)-Ag(1)*: 83.789(17)
	P(1)-N(2): 1.602(5)	Ag(3)-Ag(1)-Ag(1)*: 59.925(12)
	P(1)-N(4): 1.656(5)	N(22)*-Ag(2)-N(32): 138.8(2)
	P(1)-N(3): 1.664(5)	N(22)*-Ag(2)-N(2): 134.84(18)
		N(32)-Ag(2)-N(2): 86.31(17)
		N(22)*-Ag(2)-Ag(1): 83.59(14)
		N(32)-Ag(2)-Ag(1): 113.65(14)
		N(2)-Ag(2)-Ag(1): 75.23(10)
		N(22)*-Ag(2)-Ag(2)*: 75.18(15)
		N(32)-Ag(2)-Ag(2)*: 141.69(15)
		N(2)-Ag(2)-Ag(2)*: 62.55(11)
		Ag(1)-Ag(2)-Ag(2)*: 81.082(16)
		N(12)*-Ag(3)-N(12): 178.1(3)
		N(12)*-Ag(3)-Ag(1): 105.44(13)
		N(12)-Ag(3)-Ag(1): 76.28(13)
		N(12)*-Ag(3)-Ag(1)*: 76.29(13)
		N(12)-Ag(3)-Ag(1)*: 105.43(13)
		Ag(1)-Ag(3)-Ag(1)*: 60.15(2)

Table S2: Hydrogen bonding distances (Å) and angles (°) for the compounds **2** – **4**

Compound	**D-H...A**	**d(H...A)Ǻ**	**d(D...A)Ǻ**	**<(DHA)°**
2	N(1)-H(1)...N(2)#1	2.24(3)	3.0359(18)	177(3)
	Symmetry transformations used to generate equivalent atoms:			
	#1 -x+2,-y+1,-z			
3	N(1)-H(1)...N(32)#1	2.30	2.985(2)	136.4
	N(2)-H(2)...N(42)#2	2.00	2.7722(19)	149.0
	N(3)-H(3)...N(4)#2	2.28	3.1138(19)	164.0
	N(3)-H(3)...N(42)#2	2.66	3.361(2)	140.0
	Symmetry transformations used to generate equivalent atoms:			
	#1 x,-y+3/2,z-1/2 #2 x,-y+3/2,z+1/2			
4	N(3)-H(3N)...O(21)#1	2.142(0)	2.993(7)	169.9(0)
	N(4)-H(4N)...O(21)#1	2.201(0)	3.027(7)	161.0(0)
	Symmetry transformations used to generate equivalent atoms:			
	#1 x+1/2,-y+1,-z+1/2			

<u>Additional Figures for **2** , **3** and **4**:</u>



a

Figure S1. (a) Molecular structure of **2**.

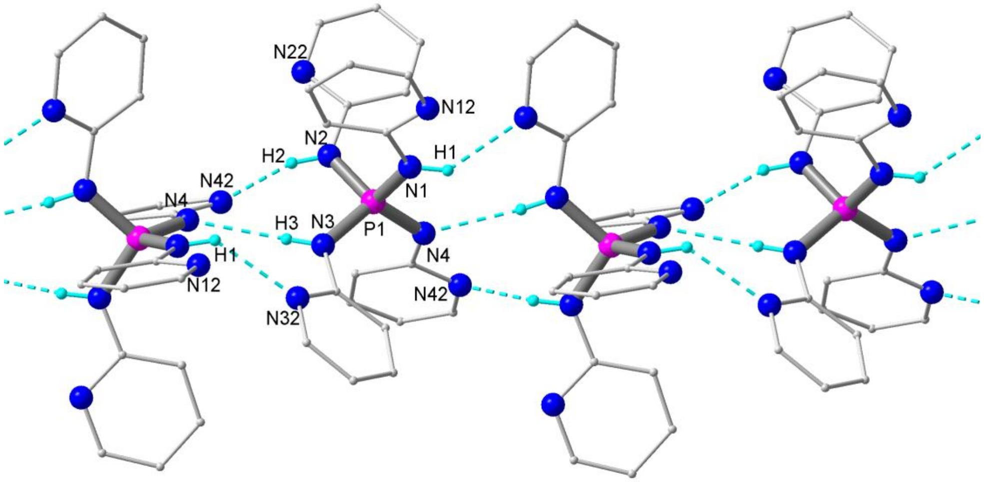


Figure S2. Formation of 1D-chain structure in **3** mediated by N-H…N interactions

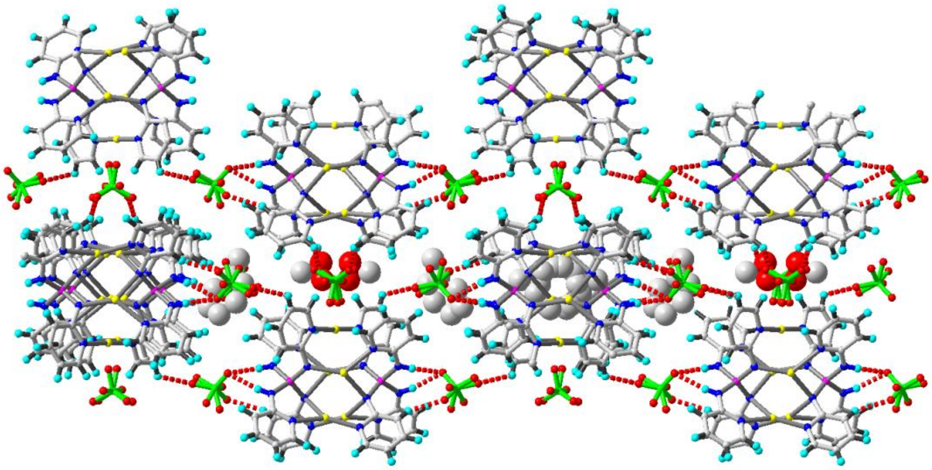


Figure S3. View down the channel structure of **4** showing the inner arrangement of solvated toluene and methanol molecules

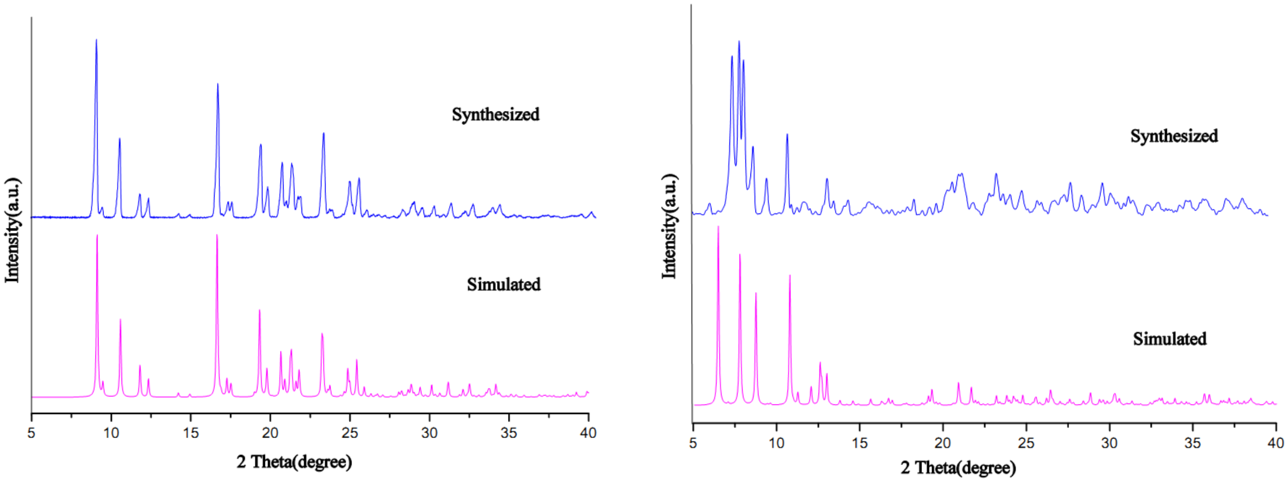


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Figure S4. PXRD pattern for **3** (left) and **4** (right). The slight mismatch of the experimental and simulated pattern for **4** is presumably due to the presence of solvated molecules in the single crystal X-ray data.

Theoretical Calculation for **1** and **3**:

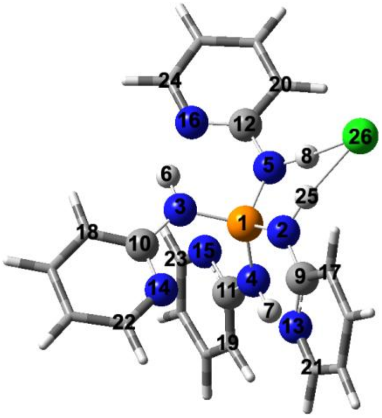


Figure S5. Optimized structure of **1**

Table S3: Optimized parameters for **1**

Parameter	**Values**
P1-N2	1.65268Å
P1-N3	1.66442Å
P1-N4	1.66444Å
P1-N5	1.65261Å
N2-H25	1.05658Å
N5-H8	1.05663Å
H25-*Cl*26	2.03875Å
H8-*Cl*26	2.03843Å
N5-H25-*Cl*26	158.10407°
N2-H8-*Cl*26	158.10403°
N13-H7	1.85984Å
N16-H6	1.85977Å
N4-H7…N13	143.69295°
N3-H6…N16	143.63515°
H8-Cl26-H25	59.57691°
C9-N2-P1-N3	100.02229°
C9-N2-P1-N4	-24.45477°
C9-N2-P1-N5	-147.10213°
P1-N2-C9-N13	9.27696°
P1-N5-C12-N16	9.29545°
N2-C9-N13-H7	8.39337°
N5-C12-N16-H6	8.38103°

Table S4: Optimized Geometries in Cartesian Coordinates for **1**

P	-0.00003395	0.44186378	-0.00005894
N	0.43603269	-0.48844790	-1.30952925
N	-0.43595854	-0.48855766	1.30936090
N	1.26891757	1.48327082	0.19120134
N	-1.26897933	1.48319328	-0.19120878
H	1.45055568	-0.42317163	-1.50590852
H	-1.45045354	-0.42318233	1.50590608
H	0.94619930	2.47493490	0.36095471
H	-0.94631330	2.47491866	-0.36098657
C	-0.32247869	-1.52374371	-1.85551469
N	-1.59671379	-1.60067463	-1.45804215
C	-2.36060592	-2.56927423	-1.98280338
C	-1.90058437	-3.49119640	-2.91991961
C	-0.56405584	-3.39837898	-3.32717744
C	0.24720019	-2.40600970	-2.79216816
C	0.32264867	-1.52370940	1.85545661
N	1.59686086	-1.60065406	1.45789699
C	2.36083498	-2.56912140	1.98276779
C	1.90093431	-3.49090799	2.92008273
C	0.56443581	-3.39808216	3.32742749
C	-0.24690925	-2.40584240	2.79230790
C	2.62066013	1.39465667	-0.17844160
N	3.03155110	0.39564921	-0.96833738
C	4.33131747	0.34254046	-1.30672086
C	5.26782366	1.28279739	-0.89752911
C	4.82338669	2.34142584	-0.09323273
C	3.48952390	2.40377531	0.27996436
C	-2.62073560	1.39443935	0.17840716
N	-3.03148191	0.39550094	0.96846960
C	-4.33124268	0.34225064	1.30684449
C	-5.26787958	1.28231082	0.89748664
C	-4.82359354	2.34086653	0.09301956
C	-3.48973153	2.40334570	-0.28018142
H	-3.39032770	-2.59737798	-1.63343209
H	-2.56314926	-4.25209161	-3.31778125
H	-0.15888316	-4.09536151	-4.05502735
H	1.28742986	-2.30471662	-3.08388762
H	3.39053148	-2.59724412	1.63332047
H	2.56357333	-4.25169675	3.31802389
H	0.15934521	-4.09495060	4.05543227
H	-1.28712016	-2.30454908	3.08409610
H	4.61875105	-0.49052348	-1.94388158
H	6.30454302	1.19774628	-1.20429024
H	5.51455664	3.10931720	0.24123662
H	3.10264845	3.20857301	0.89511488
H	-4.61856823	-0.49075012	1.94413581
H	-6.30458869	1.19715703	1.20425480
H	-5.51487314	3.10860094	-0.24158308
H	-3.10295677	3.20809122	-0.89546098
Cl	-0.00045201	4.24414740	0.00008908

Table S5: Optimized Geometries in Cartesian Coordinates for **3**

P	0.00000000	0.00000000	0.00000000
N	0.00000000	0.00000000	1.57259501
N	1.46738400	0.00000000	-0.81249952
N	-1.00654510	1.21729937	-0.58672040
N	-0.58664326	-1.53389802	-0.44689420
H	1.57079592	-0.75750606	-1.50143700
H	-1.24778494	1.86375555	0.18282114
H	-1.31795040	-1.82133395	0.19237213
C	-0.35171273	0.98321939	2.46214147
N	-1.03979299	2.08534804	2.07118686
C	-1.37635681	3.00330611	2.99133090
C	-1.07104204	2.89866022	4.34286422
C	-0.36559244	1.75804407	4.75870318
C	-0.00494297	0.80083925	3.82622173
C	2.37379821	1.05353857	-0.80844639
N	2.07981707	2.10552314	-0.03460299
C	2.95056767	3.12350984	0.00017366
C	4.13922303	3.15190876	-0.72538019
C	4.43365839	2.04798223	-1.53597917
C	3.54850002	0.98005761	-1.58508645
C	-1.28230234	1.56604842	-1.90055615
N	-0.92011173	0.69984790	-2.85726805
C	-1.19589470	1.01880419	-4.13018936
C	-1.84255939	2.18954109	-4.51649171
C	-2.22006897	3.08677184	-3.50803871
C	-1.93930296	2.78318639	-2.18403464
C	-0.39367318	-2.38658382	-1.53299500
N	0.71070633	-2.24977787	-2.27879157
C	0.89871702	-3.09127834	-3.30678637
C	0.02254099	-4.11965146	-3.63322722
C	-1.12367070	-4.27070660	-2.84129927
C	-1.34394121	-3.39927436	-1.78587193
H	-1.92370010	3.86677607	2.61602219
H	-1.37112332	3.67296901	5.04074510
H	-0.09993745	1.62564337	5.80440897
H	0.54497782	-0.09185153	4.10259631
H	2.67388399	3.95516467	0.64487893
H	4.80807896	4.00325679	-0.65933856
H	5.34777485	2.02134939	-2.12249045
H	3.74819800	0.10655179	-2.19763071
H	-0.88139911	0.28961825	-4.87450635
H	-2.04274474	2.39267305	-5.56302262
H	-2.72487674	4.01632775	-3.75596845
H	-2.20984211	3.45787810	-1.37809995
H	1.80579841	-2.93032253	-3.88502064
H	0.22777664	-4.77711508	-4.47068921
H	-1.84272994	-5.05667092	-3.05342595
H	-2.23294200	-3.48058332	-1.16788389

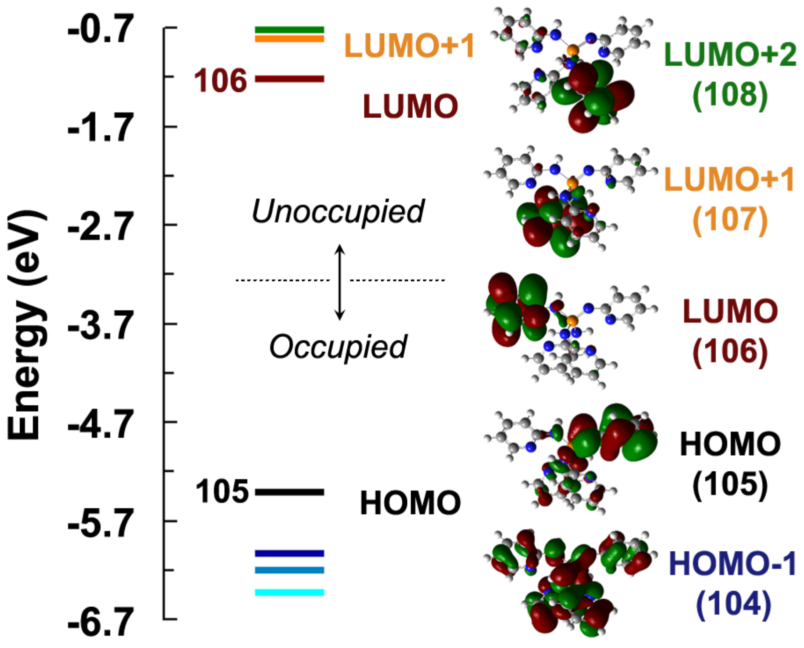
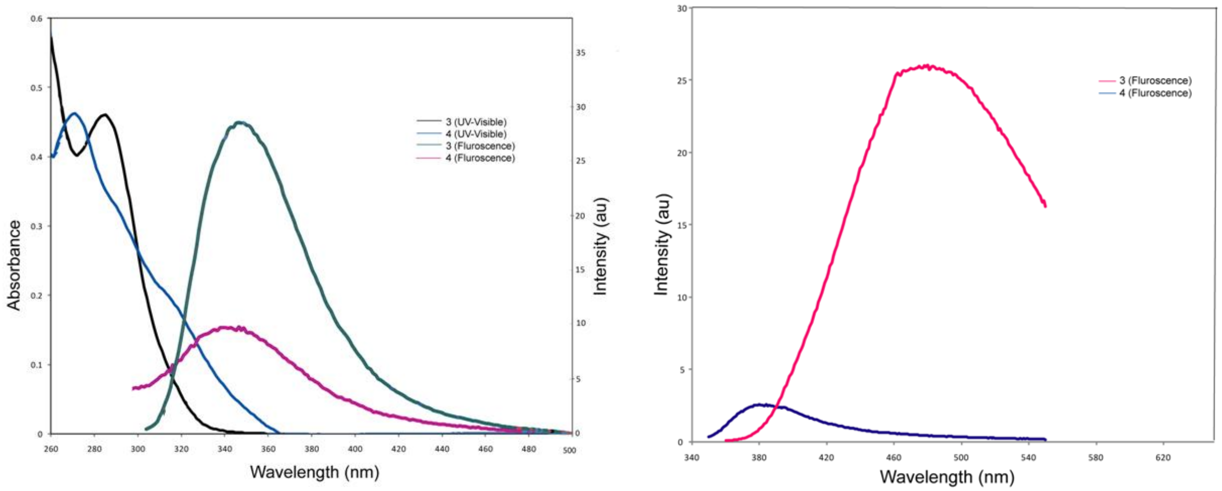


Figure S6. Density Functional Theory (DFT) derived molecular orbital energy levels of **3**



a b

Figure S7. (a) UV-Visible and Emission spectra of **3** and **4** in DMSO. (b) Solid-State emission spectra taken on the front face mode

The UV-visible spectrum of **3** in DMSO shows a single absorption at ~284nm (Figure S7a) and is largely different from that obtained in methanol which gave four different peaks at 230nm, 255nm, 290nm and 320nm (please refer to the figure in the main text). The transitions in methanol are due to the pyridyl chromophore's ($n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$) transitions as well as due to their interactions with the solvent methanol. On the other hand, such solvent interactions are absent in DMSO (aprotic polar) giving rise to only a single absorption. The UV-visible spectrum of the complex **4** is blue-shifted compared to **3** and absorbs at ~270nm. It is also worthwhile to note a low energy band at ~315nm indicating different kinds of transitions involving amino and metal bound imido groups in **4**. The emission signatures of **3** and **4** have vibronic structures and show their values at 354 (λ_{ex} = 365 nm) and 350 nm (λ_{ex} = 307 nm), respectively. Further, the fluorescence intensity of **4** is fairly quenched and somewhat blue shifted from **3**. The florescence quenching is presumably due to depletion of electron densities at the imino sites caused by its coordination to Ag (I) ions. Interestingly, the solid-state fluorescence spectra of **3** and **4** shows emission bands at 480 (λ_{ex} = 364 nm) and 380 nm (λ_{ex} = 342 nm) indicating significant quenching as well as blue shift for **4** in comparison with its solution spectra (Figure S7b).

Pka calculations:

The pka of a base (or a conjugate acid) can be obtained by the Hammettes equation, which is used for the dissociation reaction of an acid in aqueous medium and given by following equation

$$\mathbf{3}H^+ + H_2O \rightleftharpoons \mathbf{3} + H_3O^+$$

Where [$3H^+$] and [3] are molar concentration of conjugate acid and base respectively. H_0 is called Hammette’s acidity function, which is given by the following reaction

The factors f_3 and $f_{3H}{}^+$ are the acidity co-efficients of the base and the conjugate acid. The parameter $a_H{}^+$ is the activity of the proton: for dilute solution H_0 is replaced by pH. A plot of pH versus

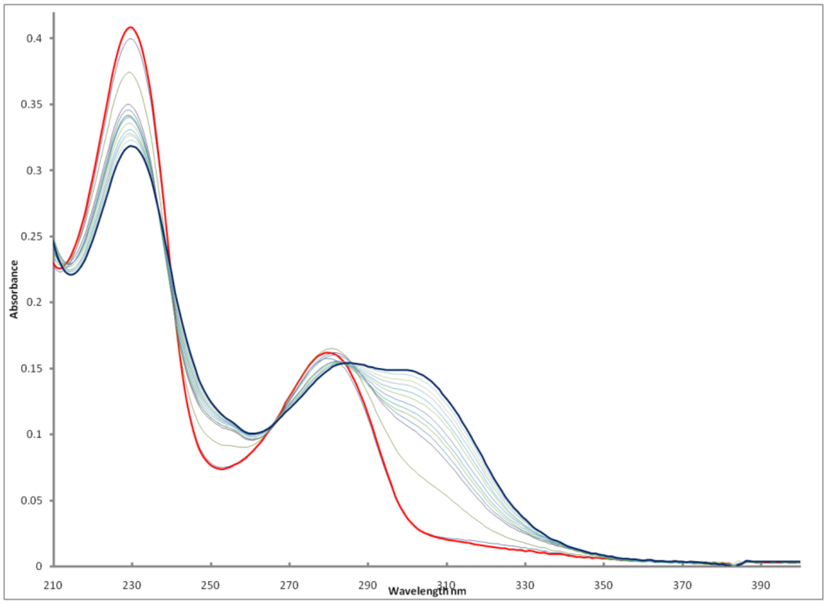
is a straight line with unit slope and *pH= pKa when [3] = [3H⁺]*. The factor can be determined from following relation.

Where $A_{3H}{}^+$ and A_3 are the absorbance (at the analytical wavelength) of the pure $3H^+$ and 3 respectively. And *A* is the absorbance (at same wavelength) of any solution in which $3H^+$ is partially ionized.

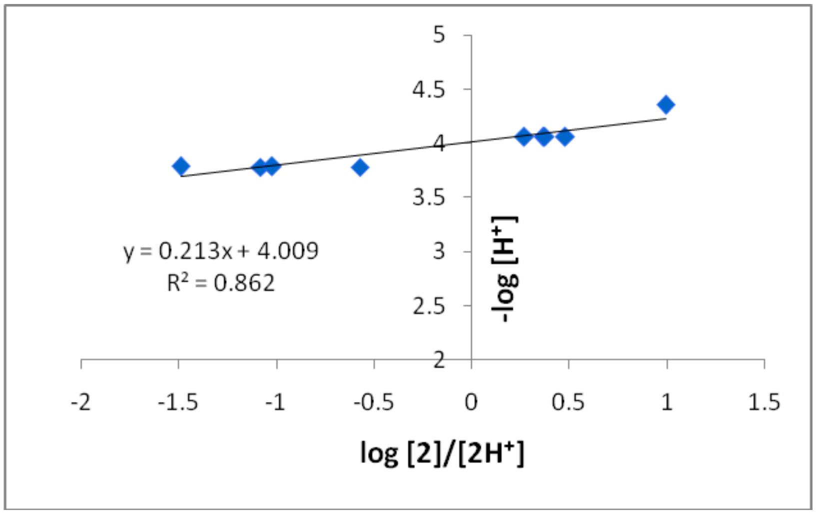
Where [C] = Molar concentration of compound in experimental solution.

ε is molar extinction coefficient. Generally two wavelengths (λ_1 andλ_2) were chosen on both side of isobestic point.

The spectral profile and the graph for Pka determination of **3** are given in the main text…..



a



b

Figure S8. (a) Parallel Titration of **2** with 0.025 M H_2SO_4 in MeOH (b) Henderson-Hammette plot for the Pka determination of **2**