

## Supporting Information

### **Syntheses, crystal structures and supramolecular assemblies of two Cu(II) complexes based on a new heterocyclic ligand: Insights through C–H...Cl and $\pi\cdots\pi$ interactions**

Samit Pramanik<sup>a</sup>, Sudipta Pathak<sup>\*,b</sup> Antonio Frontera<sup>\*,c</sup> and Subrata Mukhopadhyay<sup>a</sup>

<sup>a</sup>Department of Chemistry, Jadavpur University, Kolkata 7000032, West Bengal, India

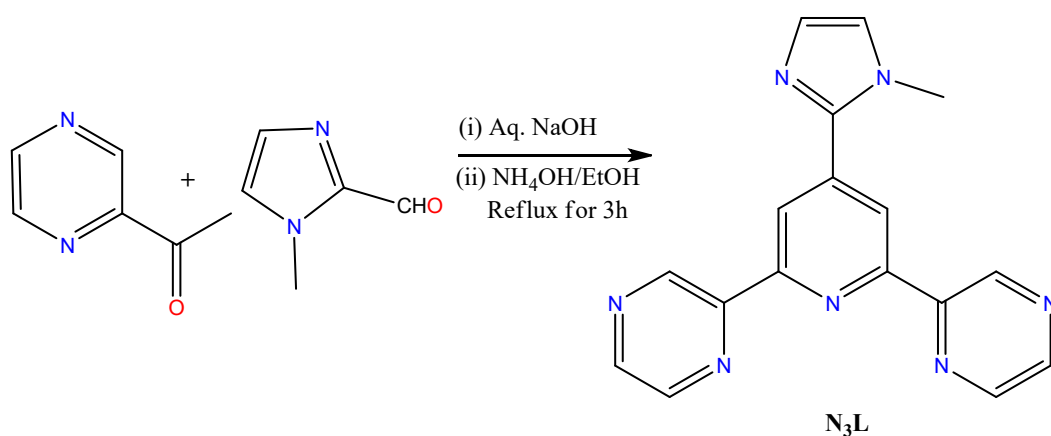
<sup>b</sup>Department of Chemistry, Haldia Government College, Debhog, Purba Medinipur 721657, West Bengal, India

<sup>c</sup>Departament de Química, Universitat de les Illes Balears, Crta. de Valldemossa km 7.5, 07122 Palma de Mallorca (Balears), Spain

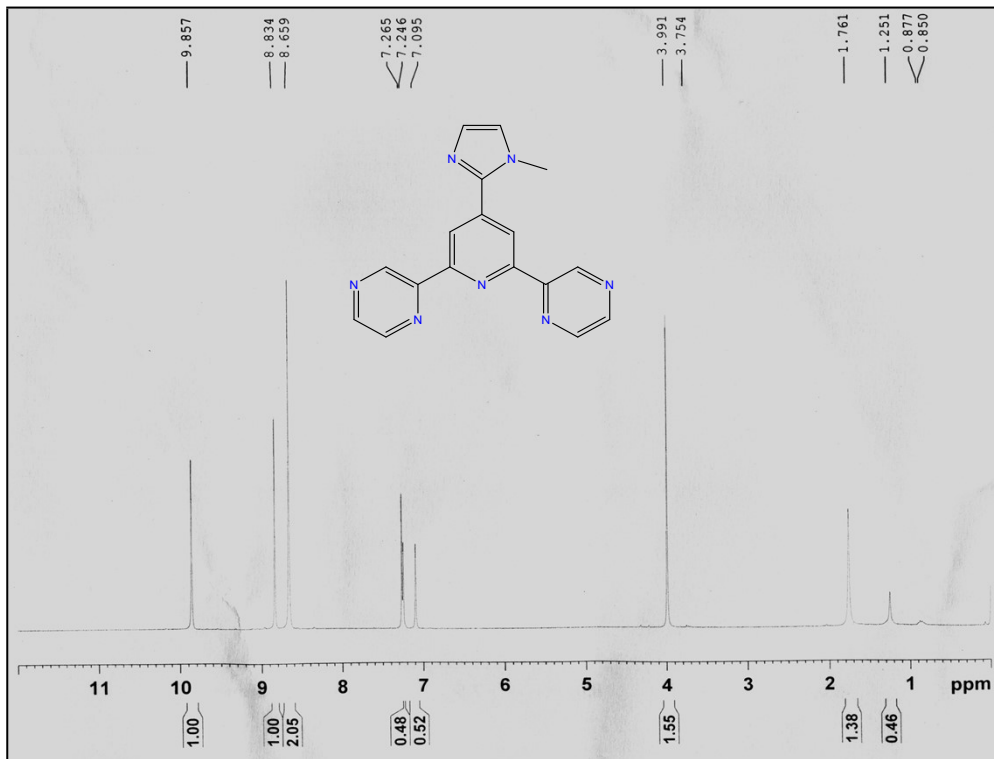
#### Table of Contents:

Sl. No.	Contents	Page No.
1.	Scheme S1 Synthetic route for the ligand, <b>N<sub>3</sub>L</b>	2
2.	Fig. S1 <sup>1</sup> H NMR spectrum of <b>N<sub>3</sub>L</b> in CDCl <sub>3</sub> solution	3
3.	Fig. S2 <sup>13</sup> C NMR spectrum of <b>N<sub>3</sub>L</b> in CDCl <sub>3</sub> solution	3
4.	Fig. S3 FT-IR spectrum of <b>N<sub>3</sub>L</b>	4
5.	Fig. S4 ESI-mass spectrum of <b>N<sub>3</sub>L</b>	4
6.	Scheme S2 Schematic representations of the synthesis of complex <b>1</b> and <b>2</b>	5
7.	Table S1 Crystal data and structure refinement parameters for Complex <b>1</b> and <b>2</b>	6
8.	Table S2 Selected bond distances [Å] for Complex <b>1</b> and <b>2</b>	7

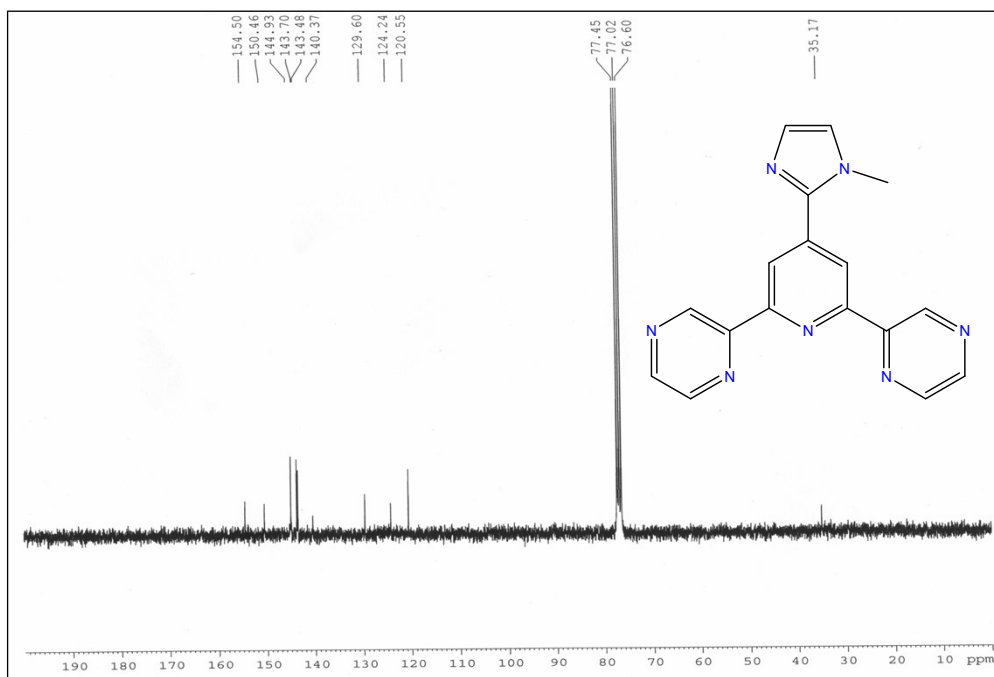
9.	Table S3 Selected bond angles [°] for Complex <b>1</b> and <b>2</b>	7
10.	Table S4 Geometrical parameters for the hydrogen bonds of Complex <b>1</b> and <b>2</b>	7–8
11.	Table S5 Geometrical parameters (Å, °) for the $\pi$ -stacking interactions for the title Complexes	8–9
12.	Fig. S5 FT-IR spectra for Complex <b>1</b> and <b>2</b>	9
13.	Tau ( $\tau$ ) parameter calculations for Complex <b>1</b> and <b>2</b>	10
14.	Fig. S6 2D architecture through C–H $\cdots$ O hydrogen bonding and intramolecular anion $\cdots\pi$ interactions in Complex <b>2</b>	10
15.	Table S6 A brief comparison of structural features of substituted terpyridine derived Cu(II) complexes	11
16.	Table S7 A brief comparison of $\pi\cdots\pi$ and C–H $\cdots$ Cl hydrogen bonding interactions in substituted terpyridine derived Cu(II) complexes	12
17.	Fig. S7 Hirshfeld surfaces mapped with (a) $d_{\text{norm}}$ (b) $d_e$ (c) $d_i$ (d) shape-index and (e) curvedness for the Complex <b>1</b> .	13
18.	Fig. S8 Hirshfeld surfaces mapped with (a) $d_{\text{norm}}$ (b) $d_e$ (c) $d_i$ (d) shape-index and (e) curvedness for the Complex <b>2</b>	13



**Scheme S1** Synthetic route for the ligand, **N<sub>3</sub>L**



**Fig. S1**  $^1H$  NMR spectrum of  $N_3L$  in CDCl<sub>3</sub> solution



**Fig. S2**  $^{13}C$  NMR spectrum of  $N_3L$  in CDCl<sub>3</sub> solution

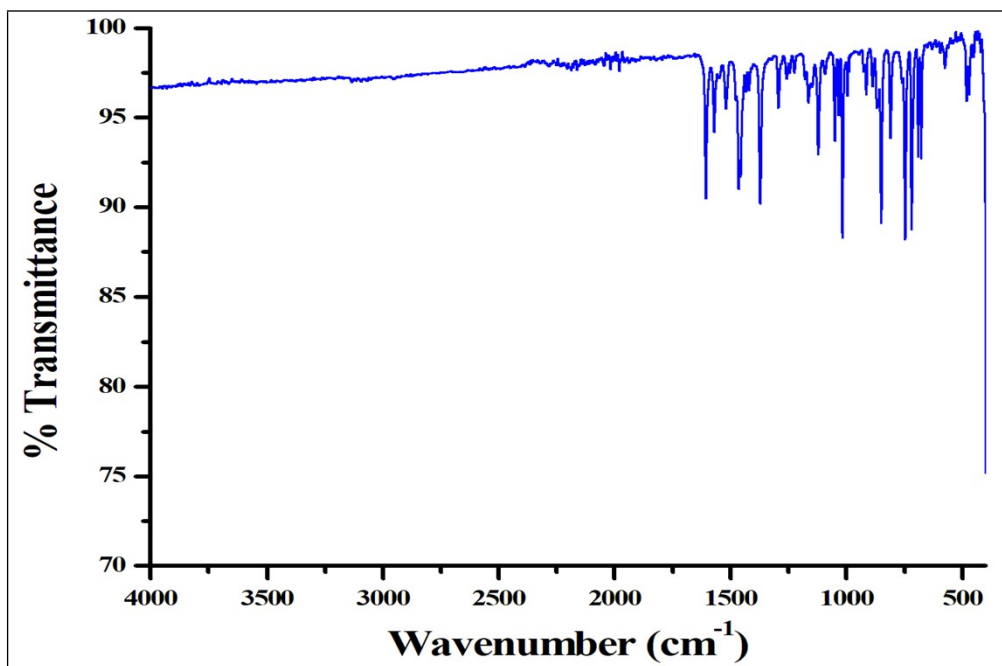


Fig. S3 FT-IR spectrum of N<sub>3</sub>L

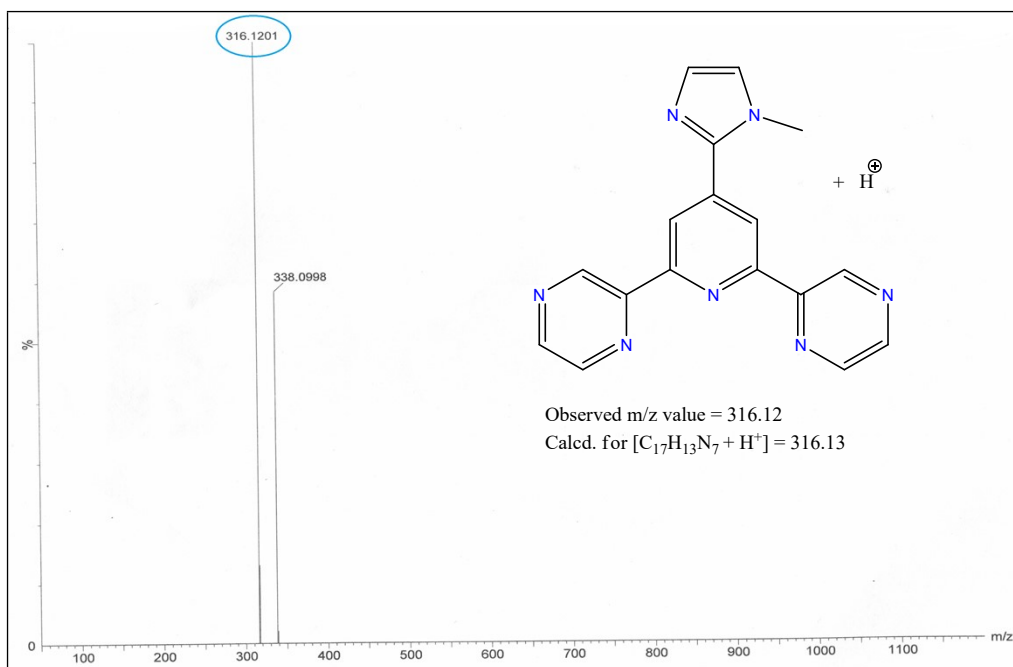
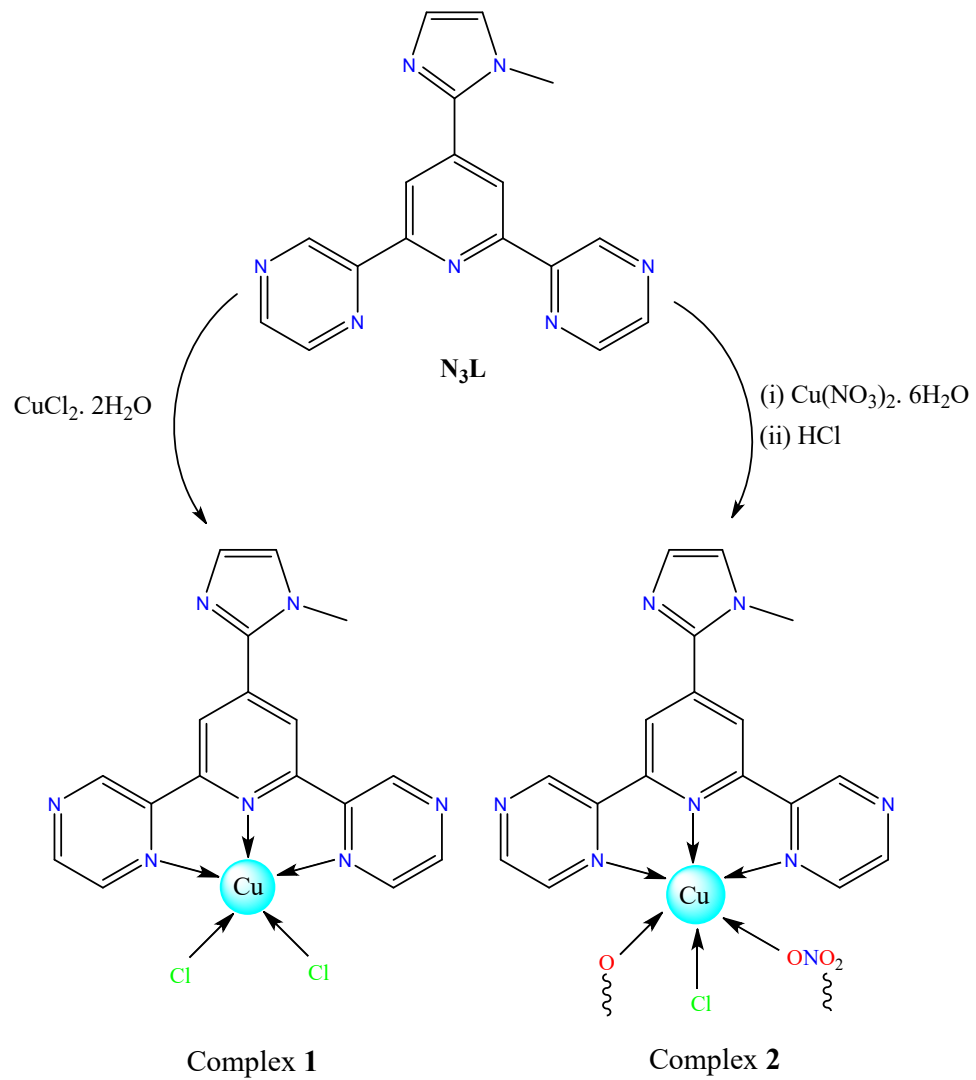


Fig. S4 ESI-mass spectrum of N<sub>3</sub>L



**Scheme S2** Schematic representations of the synthesis of complex 1 and 2

**Table S1 Crystal Data and Structure Refinement Parameters for Complex 1 and 2**

Structure	Complex 1	Complex 2
Empirical formula	C <sub>17</sub> H <sub>13</sub> N <sub>7</sub> CuCl <sub>2</sub>	C <sub>17</sub> H <sub>13</sub> N <sub>8</sub> CuClO <sub>3</sub>
Formula Weight	449.79	476.35
Temperature (K)	273(2)	273(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
space group	P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	P 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a, b, c (Å)	7.0900(5), 15.0538(11), 16.4613(12)	6.9172(9), 15.1342(19), 17.174(2)
α, β, γ (°)	90, 90, 90	90, 90, 90
Volume (Å <sup>3</sup> )	1756.9(2)	1797.9(4)
Z / Density (calc.) (Mg/m <sup>3</sup> )	4 / 1.701	4 / 1.760
Absorption coefficient (mm <sup>-1</sup> )	1.566	1.405
F(000)	908.0	964.0
Crystal size (mm <sup>3</sup> )	0.09 × 0.14 × 0.19	0.08 × 0.13 × 0.19
θ range for data collection	1.833 to 27.169	1.794 to 27.173
Completeness to θ (%)	100%	100%
Absorption correction	Multi-scan	Multi-scan
Max. and min. transmission	0.869 and 0.769	0.894 and 0.803
Refinement method	Full-matrix least-squares on F <sup>2</sup>	Full-matrix least-squares on F <sup>2</sup>
Data/parameters	3883 / 288	3979 / 272
Goodness-of-fit on F <sup>2</sup>	0.790	0.883
Final R indices [I > 2σ(I)]	R <sub>1</sub> = 0.0223, wR <sub>2</sub> = 0.0756	R <sub>1</sub> = 0.0348, wR <sub>2</sub> = 0.1067
R indices (all data)	R <sub>1</sub> = 0.0265, wR <sub>2</sub> = 0.0881	R <sub>1</sub> = 0.0383, wR <sub>2</sub> = 0.1122
Largest diff. peak and hole (e.Å <sup>-3</sup> )	0.644 and -0.850	0.485 and -0.382

$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ ,  $wR_2 = \left[ \frac{\sum \{(F_o^2 - F_c^2)^2\}}{\sum \{w(F_o^2)^2\}} \right]^{1/2}$ ,  $w = 1 / \{\sigma^2(F_o^2) + (aP)^2 + bP\}$ ,  $P = (F_o^2 + 2F_c^2) / 3$  where, a = 0.1000, b = 0.2438 for complex 1 and a = 0.1000, b = 0.8005 for complex 2.

**Table S2 Selected Bond Distances [Å] for Complex 1 and 2**

	Bonds	Distance (Å)	Bonds	Distance (Å)
Complex 1	Cu1—Cl1	2.2495(9)	Cu1—N5	1.963(2)
	Cu1—Cl2	2.3629(10)	Cu1—N6	2.064(2)
	Cu1—N4	2.051(2)		
Complex 2	Cu1—Cl1	2.1922(13)	Cu1—N5	1.938(3)
	Cu1—O1	2.498(5)	Cu1—N6	2.049(3)
	Cu1—N4	2.031(3)	Cu1—O2 b	2.641(4)

b = 1+x, y, z

**Table S3 Selected Bond Angles [°] for Complex 1 and 2**

	Bond angles	Value (°)	Bond angles	Value (°)
Complex 1	Cl1—Cu1—Cl2	110.32(3)	N4—Cu1—N6	157.23(10)
	Cl1—Cu1—N4	94.99(8)	N5—Cu1—N6	78.79(9)
	Cl1—Cu1—N5	144.19(7)	Cu1—N4—C8	114.12(19)
	Cl1—Cu1—N6	99.45(8)	Cu1—N4—C11	127.3(2)
	Cl2—Cu1—N4	97.91(8)	Cu1—N5—C7	119.24(18)
	Cl2—Cu1—N5	105.48(7)	Cu1—N5—C16	119.47(18)
	Cl2—Cu1—N6	93.48(8)	Cu1—N6—C12	127.3(2)
	N4—Cu1—N5	79.20(9)	Cu1—N6—C15	113.67(19)
Complex 2	Cl1—Cu1—O1	102.68(12)	N5—Cu1—N6	79.67(13)
	Cl1—Cu1—N4	97.18(10)	O2 b—Cu1—N5	81.91(18)
	Cl1—Cu1—N5	170.47(11)	O2 b—Cu1—N6	73.88(17)
	Cl1—Cu1—N6	103.20(10)	Cu1—O1—N8	122.8(3)
	Cl1—Cu1—O2 b	90.11(15)	Cu1 a—O2—N8	131.5(4)
	O1—Cu1—N4	97.98(15)	Cu1—N4—C8	113.6(3)
	O1—Cu1—N5	86.77(15)	Cu1—N4—C11	128.2(3)
	O1—Cu1—N6	79.06(14)	Cu1—N5—C7	118.9(2)
	O1—Cu1—O2 b	152.10(17)	Cu1—N5—C16	119.5(3)
	N4—Cu1—N5	79.98(13)	Cu1—N6—C12	127.5(3)
	N4—Cu1—N6	159.58(13)	Cu1—N6—C15	113.7(3)
O2 b—Cu1—N4	104.97(17)			

a = -1+x, y, z; b = 1+x, y, z

**Table S4 Geometrical Parameters for the Hydrogen Bonds of Complex 1 and 2**

	D—H···A	D—H [Å]	H···A	D···A [Å]	D—H···A [°]	Symmetry
	C6—H6···Cl1	0.9300	2.8200	3.741(3)	171.00	1/2-x, 1-y, -1/2+z

Complex 1	C9—H9···C11	0.92(3)	2.55(3)	3.464(3)	176(3)	1/2-x, 1-y, -1/2+z
	C10—H10···C12	0.97(5)	2.76(5)	3.567(3)	142(4)	1-x, -1/2+y, 3/2-z
	C13—H13···C12	0.98(3)	2.83(3)	3.770(3)	162(3)	-1/2+x, 3/2-y, 2-z
	C14—H14···C11	0.99(5)	2.80(5)	3.651(3)	145(4)	-x, 1/2+y, 3/2-z
	C17—H17···C11	0.93(4)	2.81(4)	3.682(3)	157(3)	-x, 1/2+y, 3/2-z
Complex 2	C1—H1B···C11	0.9600	2.7600	3.611(6)	148.00	2-x, 1/2+y, 1/2-z
	C9—H9···C11	0.9300	2.4900	3.409(5)	168.00	3/2-x, 1-y, 1/2+z
	C3—H3···O2	0.9300	2.5500	3.221(8)	129.00	1/2+x, 3/2-y, 1-z
	C14—H14···O3	0.9300	2.2300	3.073(7)	151.00	1-x, 1/2+y, 1/2-z

**Table S5 Geometrical Parameters (Å, °) for the  $\pi$ -Stacking Interactions for the Title Complexes**

	Cg(i)···Cg(j)	Cg(i)··· Cg(j)[ Å]	$\alpha$ (°)	$\beta$ (°)	$\gamma$ (°)	Cg(i)– perp[Å ]	Cg(j)– perp[Å ]	Symmetry
Complex 1	Cg(3)[1]···Cg(5)	3.6866(18)	2.71	25.2 9	26.0 0	3.313	3.333	-1/2+x, 3/2-y, 1-z
	Cg(3)[1]···Cg(5)	3.5021(18)	2.71	11.4 0	10.1 7	3.447	3.433	1/2+x, 3/2-y, 1-z
	Cg(4)[1]···Cg(6)	3.958(2)	22.8 0	19.2 0	41.0 5	2.985	3.738	-x, -1/2+y, 3/2-z
	Cg(5)[1]···Cg(3)	3.5020(18)	2.71	10.1 7	11.4 0	3.433	3.447	-1/2+x, 3/2-y, 1-z
	Cg(5)[1]···Cg(3)	3.6867(18)	2.71	26.0 0	25.2 9	3.333	3.313	1/2+x, 3/2-y, 1-z
	Cg(6)[1]···Cg(4)	3.958(2)	22.8 0	41.0 5	19.2 0	3.738	2.985	-x, 1/2+y, 3/2-z



Complex 2	Cg(3)[1]⋯Cg(5)	3.733(3)	8.82	21.6	19.5	3.518	3.470	-1/2+x, 3/2-y, 1-z
	Cg(3)[1]⋯Cg(5)	3.905(3)	8.82	35.7	31.6	3.323	3.170	1/2+x, 3/2-y, 1-z
	Cg(4)[1]⋯Cg(6)	3.826(3)	12.8	22.3	34.2	3.161	3.539	2-x, -1/2+y, 1/2-z
	Cg(5)[1]Cg⋯(3)	3.905(3)	8.82	31.6	3.17	35.72	3.323	-1/2+x, 3/2-y, 1-z
	Cg(5)[1]⋯Cg(3)	3.733(3)	8.82	19.5	21.6	3.470	3.518	1/2+x, 3/2-y, 1-z
	Cg(6)[1]⋯Cg(4)	3.825(3)	12.8	34.2	22.3	3.538	3.160	2-x, 1/2+y, 1/2-z

Cg(i) and Cg(j) denotes centroid of  $i^{\text{th}}$  and  $j^{\text{th}}$  ring respectively. For Complex 1: Cg(3) is the centroid of [N1/C2/C3/N2/C4] ring; Cg(4) is the centroid of [N3/C9/C8/N4/C11/C10] ring; Cg(5) is the centroid of [N5/C7/C6/C5/C17/C16] ring; and Cg(6) is the centroid of [N6/C12/C13/N7/C14/C15] ring. For Complex 2: Cg(3) is the centroid of [N1/C2/C3/N2/C4] ring; Cg(4) is the centroid of [N3/C9/C8/N4/C11/C10] ring; Cg(5) is the centroid of [N5/C7/C6/C5/C17/C16] ring; and Cg(6) is the centroid of [N6/C12/C13/N7/C14/C15] ring.

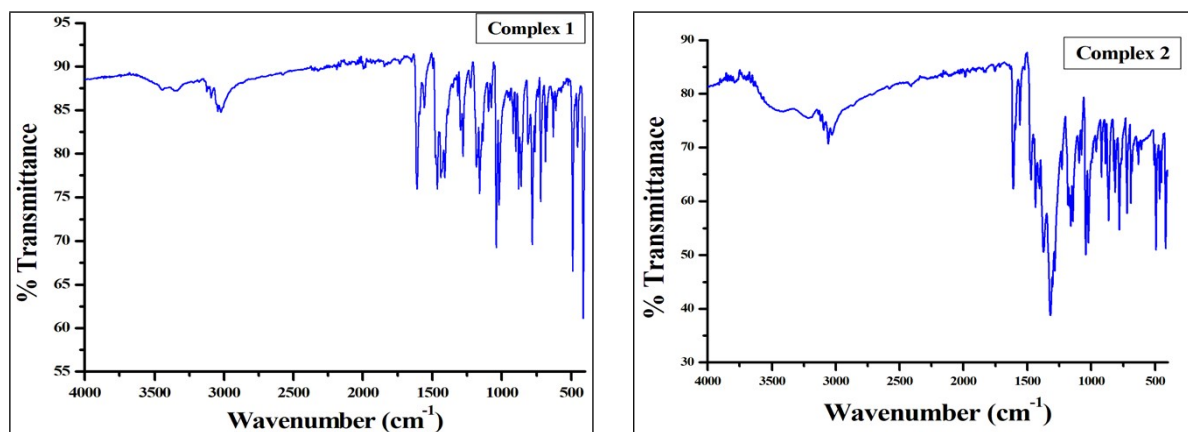


Fig. S5 FT-IR spectra for Complex 1 and 2

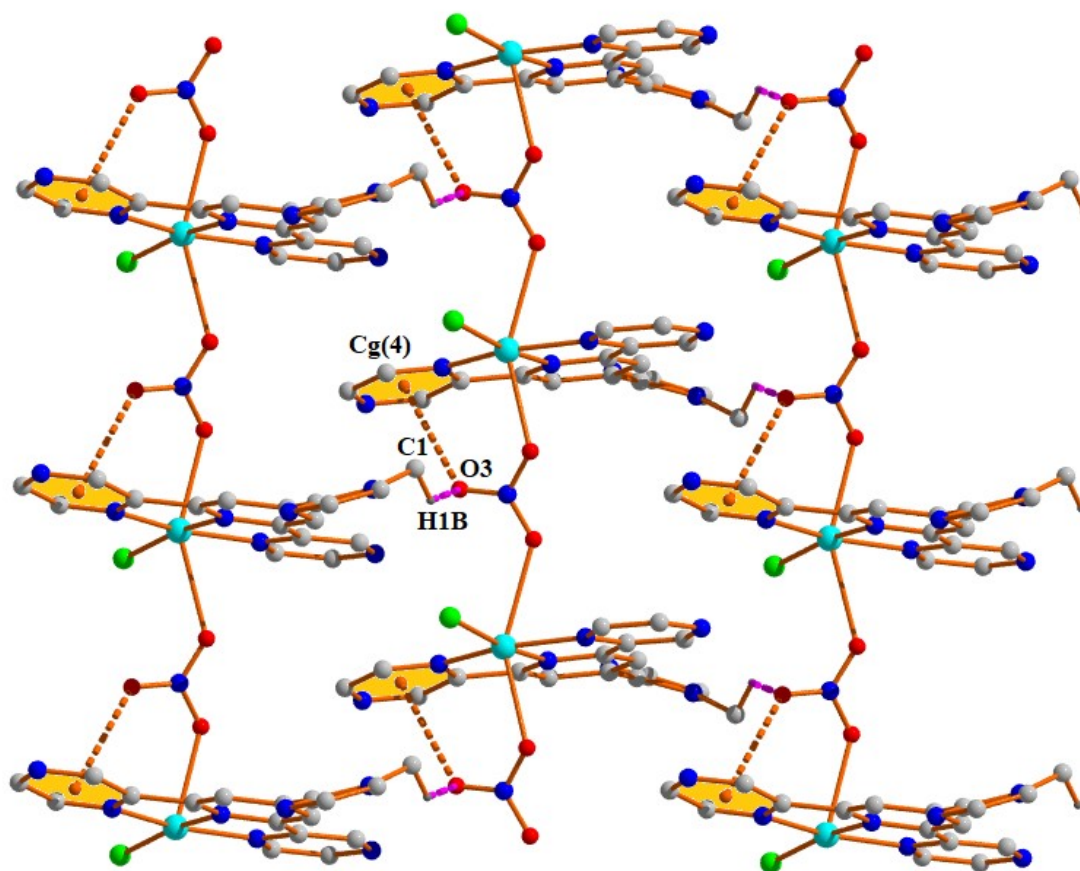
### Tau ( $\tau$ ) parameter calculation for complex 1

The structures with five coordination number can have either square pyramidal or triangular bipyramidal geometry around the metal center. In order to discriminate between these two geometries, tau ( $\tau$ ) parameter was proposed by Addison and co-workers. According to this, the  $\tau$  parameter ranges between 0 and 1 at the extreme values giving a perfect square pyramidal and triangular bipyramidal structures, respectively. The closer the  $\tau$  parameter to 0, the more similar it is to square pyramidal geometry.

$$\tau = (\beta - \alpha) / 60 \dots\dots\dots (S1)$$

Where,  $\beta$  is the first greatest angle and  $\alpha$  is the second greatest angle of the coordination center.

For complex 1:  $\beta = 157.23(10)$ , and  $\alpha = 144.19(7)$  (Table S3). Hence, calculated value of  $\tau = 0.217$ .



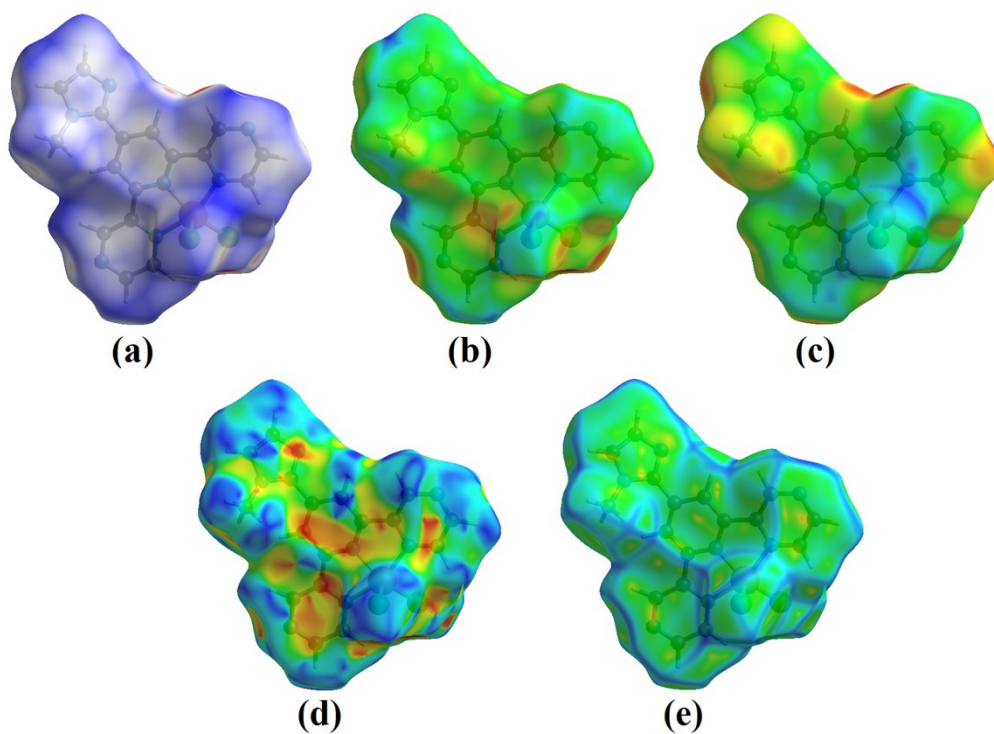
**Fig. S6** Perspective view of 2D architecture through C–H $\cdots$ O hydrogen bonding and intramolecular anion $\cdots\pi$  interactions in complex 2 (other aromatic H atoms have been omitted for clarity).

**Table S6 A brief comparison of structural features of substituted terpyridine derived Cu(II) complexes**

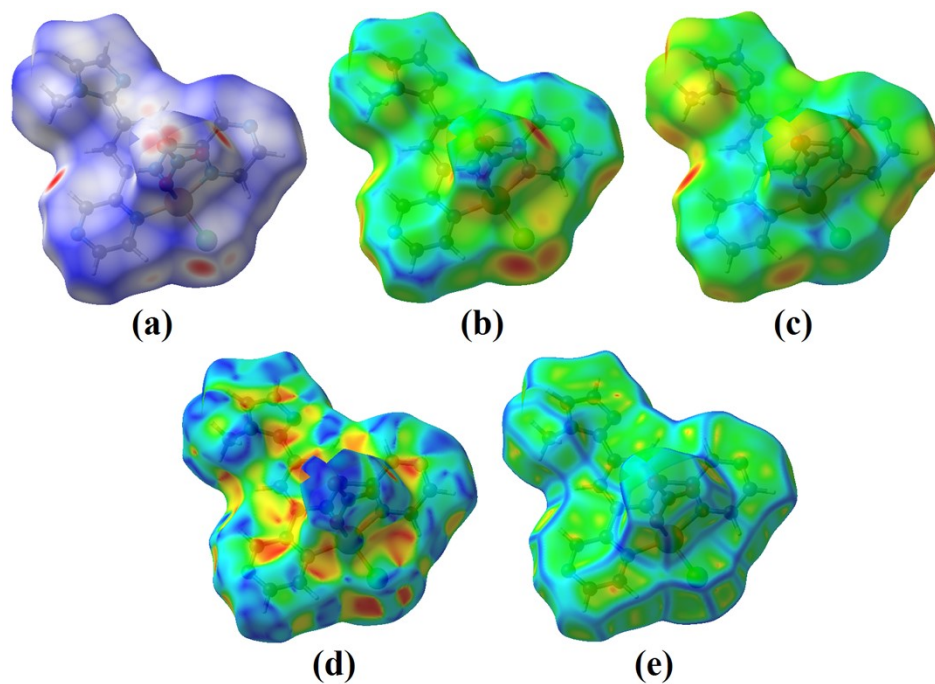
<b>Complex</b>	<b>Geometry</b>	<b>Donor chromophore(s)</b>	<b>Axial bond length(s) (Å)</b>	<b>Shifting of central metal from basal plane (Å)</b>	<b>Reference</b>
C <sub>20</sub> H <sub>15</sub> Cl <sub>2</sub> CuN <sub>7</sub> ( <b>3</b> )	Square pyradimal (τ=0.018)	N <sub>3</sub> Cl <sub>2</sub>	2.421	0.320	65
C <sub>38</sub> H <sub>26</sub> Cl <sub>6</sub> Cu <sub>3</sub> N <sub>10</sub> ( <b>4</b> )	Square pyradimal (τ=0.013) and square planner	N <sub>3</sub> Cl <sub>2</sub> and N <sub>2</sub> Cl <sub>2</sub>	2.491	0.310	66
C <sub>20</sub> H <sub>12</sub> ClCuN <sub>5</sub> O <sub>2</sub> , 2.25(H <sub>2</sub> O) ( <b>5</b> )	Square pyradimal (τ=0.27)	N <sub>3</sub> OCl	2.507	0.117	67
C <sub>18</sub> H <sub>12</sub> Cl <sub>2</sub> CuN <sub>6</sub> ( <b>6</b> )	Square pyradimal (τ=0.034)	N <sub>3</sub> Cl <sub>2</sub>	2.464	0.328	68
C <sub>18</sub> H <sub>12</sub> Cl <sub>2</sub> CuN <sub>6</sub> ( <b>7</b> )	Square pyradimal (τ=0.064)	N <sub>3</sub> Cl <sub>2</sub>	2.443	0.353	68
C <sub>22</sub> H <sub>16</sub> Cl <sub>2</sub> CuN <sub>6</sub> O ( <b>8</b> )	Square pyradimal (τ=0.014)	N <sub>3</sub> Cl <sub>2</sub>	2.508	0.316	38
C <sub>23</sub> H <sub>18</sub> Cl <sub>2</sub> CuN <sub>6</sub> O ( <b>9</b> )	Square pyradimal (τ=0.090)	N <sub>3</sub> Cl <sub>2</sub>	2.444	0.335	38
C <sub>17</sub> H <sub>13</sub> N <sub>7</sub> CuCl <sub>2</sub> ( <b>1</b> )	Square pyradimal (τ=0.217)	N <sub>3</sub> Cl <sub>2</sub>	2.363	0.437	Present work
C <sub>17</sub> H <sub>13</sub> N <sub>8</sub> CuClO <sub>3</sub> ( <b>2</b> )	Distorted octahedral	N <sub>3</sub> O <sub>2</sub> Cl	2.498 and 2.641	0.082	Present work

**Table S7 A brief comparison of  $\pi\cdots\pi$  and C–H $\cdots$ Cl hydrogen bonding interactions in substituted terpyridine derived Cu(II) complexes**

<b>Complex</b>	<b><math>\pi\cdots\pi</math> distance(s) (Å)</b>	<b>H<math>\cdots</math>Cl distance(s) (Å)</b>	<b>References</b>
C <sub>20</sub> H <sub>15</sub> Cl <sub>2</sub> CuN <sub>7</sub> ( <b>3</b> )	3.6894(16), 3.6139(17), 3.5590(18), 3.8731(18)	2.8200, 2.5900, 2.7600, 2.4400	65
C <sub>38</sub> H <sub>26</sub> Cl <sub>6</sub> Cu <sub>3</sub> N <sub>10</sub> ( <b>4</b> )	3.377(3), 3.891(3), 3.908(3), 3.851(3)	2.7900, 2.8000, 2.6500, 2.5400	66
C <sub>20</sub> H <sub>12</sub> ClCuN <sub>5</sub> O <sub>2</sub> , 2.25(H <sub>2</sub> O) ( <b>5</b> )	3.7762(17)	2.6700	67
C <sub>18</sub> H <sub>12</sub> Cl <sub>2</sub> CuN <sub>6</sub> ( <b>6</b> )	3.518(3)	2.6500, 2.6700, 2.7300, 2.6200	68
C <sub>18</sub> H <sub>12</sub> Cl <sub>2</sub> CuN <sub>6</sub> ( <b>7</b> )	3.524(5), 3.815(4), 3.781(5), 3.740(5)	2.7300, 2.7800, 2.6600	68
C <sub>22</sub> H <sub>16</sub> Cl <sub>2</sub> CuN <sub>6</sub> O ( <b>8</b> )	3.6577(18), 3.8775(16), 3.6104(15)	2.7400, 2.7600, 2.8000	38
C <sub>23</sub> H <sub>18</sub> Cl <sub>2</sub> CuN <sub>6</sub> O ( <b>9</b> )	3.9847(13), 3.9986(14), 3.8486(15)	2.6100, 2.7100, 2.8200,	38
C <sub>17</sub> H <sub>13</sub> N <sub>7</sub> CuCl <sub>2</sub> ( <b>1</b> )	3.5020(18), 3.6867(18), 3.958(2)	2.55(3), 2.76(5), 2.80(5), 2.8200	Present work
C <sub>17</sub> H <sub>13</sub> N <sub>8</sub> CuClO <sub>3</sub> ( <b>2</b> )	3.733(3), 3.826(3), 3.905(3)	2.4900, 2.7600	Present work



**Fig. S7** Hirshfeld surfaces mapped with (a)  $d_{\text{norm}}$  (b)  $d_e$  (c)  $d_i$  (d) shape-index and (e) curvedness for the complex **1**.



**Fig. S8** Hirshfeld surfaces mapped with (a)  $d_{\text{norm}}$  (b)  $d_e$  (c)  $d_i$  (d) shape-index and (e) curvedness for the complex **2**.