Electronic Supplementary Information (ESI)
(11 pages)

Photodimerization of 1D Hydrogen-bonded Zwitter ionic Lead(II) complex and its isomerization in solution

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Experimental procedure and additional characterization

$[Pb(bpe\text{-}H)_2(O_2CCF_3)_4]$, 1: IR (KBr, cm^{-1}): ν = 3447(w), 3104(w), 3054(w), 1685(s), 1631(s), 1599(s), 1507(m), 1411(m), 1182(s), 1134(s), 1000(m), 966(m), 837(m), 721(s), 544(m). ^{13}C NMR (300 MHz, D_6-DMSO, 298K, TMS): 148.03 (C-Py), 146.41 (C-Py), 132.31 (C=C), 122.67(C-Py) (Figure, ESI-8).

$[Pb(bpe\text{-}H)_2(O_2CCF_3)_4]$, 1 after UV irradiation

2. IR (KBr, cm^{-1}): ν = 3446(m), 3096(w), 1682(s), 1638(m), 1606(m) 1507(m) 1428(m), 1206(s), 1133(s), 836(m), 802(m), 723(m), 548(w). ^{13}C NMR (300 MHz, D_6-DMSO, 298K, TMS): 151.52 (C-Py, **a**), 146.57 (C-Py, **a**), 124.34 (C-Py, **a**), 44.48 (C-C, **a**) (Figure, ESI-10). ESI-MS: (m/z): (%): 365(100) $[M^+\text{-}H]$. The photo irradiated lead complex, **2** was washed with diethylether yielded white solid which was dried in vacuo to remove TFA completely.

^1H NMR (300 MHz, D_6-DMSO, 298K, TMS) of **2** after 4 days: δ = 8.58 (d, 2H, Py-H, **c**), 8.52 (d, 8H, Py-H, **b**), 8.35 (dd, 4H+ 8H, Py-H, **a** and **c** overlaps), 8.13 (d, 2H, Py-H, **c**), 7.70 (d, 2H, Py-H, **c**), 7.44 (d, 8H, Py-H, **b**), 7.25 (d, 8H, Py-H, **a**), 7.18 (d, 4H, Py-H, **c**), 6.98 (d, 2H, Py-H, **c**), 5.09 (t, 1H, CH-CH, **c**), 4.69 (s, 4H, CH-CH, **a**), 4.63 (t, 1H, CH-CH, **c**), 4.50 (t, 2H, CH-CH, **c**), 3.88 (s, 4H, CH-CH, **b**) ^{13}C NMR (D_6-DMSO, 300 MHz, 298K): 151.52 (C-Py, **a**), 151.21 (C-Py, **c**), 149.00 (C-Py, **c**), 147.42 (C-Py, **b**), 148.06 (C-Py, **a**) 125.87 (C-Py, **c**), 124.64 (C-Py, **a**), 123.69 (C-Py, **b**), 48.74(C-C, **b**), 45.42(C-C, **c**), 44.36(C-C, **a**).

Synthesis of $[Pb(rctt\text{-}tpcb)(O_2CCF_3)_2]$ and $[Pb(rctt\text{-}tpcb)(O_2CCF_3)_2]$

2a & **3**. Diethylether was layered over 2 mL methanolic solution of the irradiated powder **2**. A mixture of creamy long blocks (**3**) and yellow crystals with diamond-like faceted (**2a**)

crystals were formed after four days. (**2a**): IR (KBr, cm^{-1}): ν = 3422(m), 3064(w), 2925(w), 1683(s), 1654(m), 1602(m), 1559(w), 1418(m), 1183(s), 1134(s), 1068(w), 1001(w), 834(m), 720(m), 553(w). Creamy long blocks (**3**): IR (KBr, cm^{-1}): ν = 2926(w), 2326(w), 1676(s), 1605(s) 1559(m) 1428(m), 1197(s), 1131(s), 1066(m), 1009(m), 828(m), 723(w) 558(w).

X-ray Crystallography:

Crystal **1**: The F atoms were disordered. Four disordered models were resolved for each CF_3 group. The geometry was restrained by using SADI and isotropic thermal parameters were refined for each model. The occupancy factor was fixed at 0.25 for each model and was not refined. The 4,4'-bipyridylethylene-H is also found to be disordered. The occupancy of two disordered models were refined to 0.62(2) and 0.38(2). Only individual isotropic thermal parameters were refined for non-hydrogen atoms. All the hydrogen atoms were placed in ideal positions using AFIX option. The 405 restraints in CIF were due to this.

Crystal **2a**: The F atoms in CF_3 group were found to be disordered. Two models were resolved and DFIX option was used to constraint the geometry. The occupancy was fixed at 0.5 and not refined. The 13 restraints in CIF were due to this.

Crystal **3**: The F atoms in the two CF3 groups were disordered. Two disordered models were resolved with fixed occupancy of 0.5 and included in the refinement cycles. Only isotropic thermal parameters were refined for these F atoms. The 90 restraints in CIF were due to this.

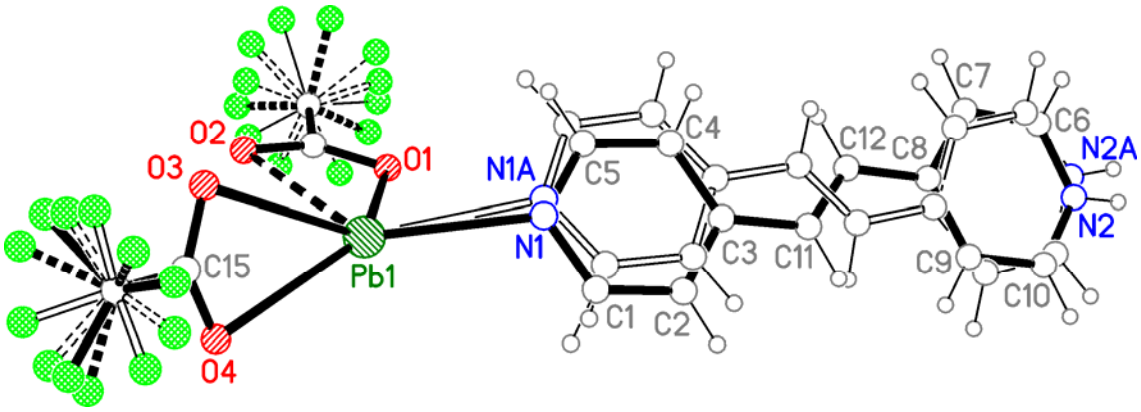


Figure ESI-1: The asymmetric unit of $[Pb(bpe\text{-}H)_2(O_2CCF_3)_4]$, **1** showing the numbering scheme and various disorders present in **1**.

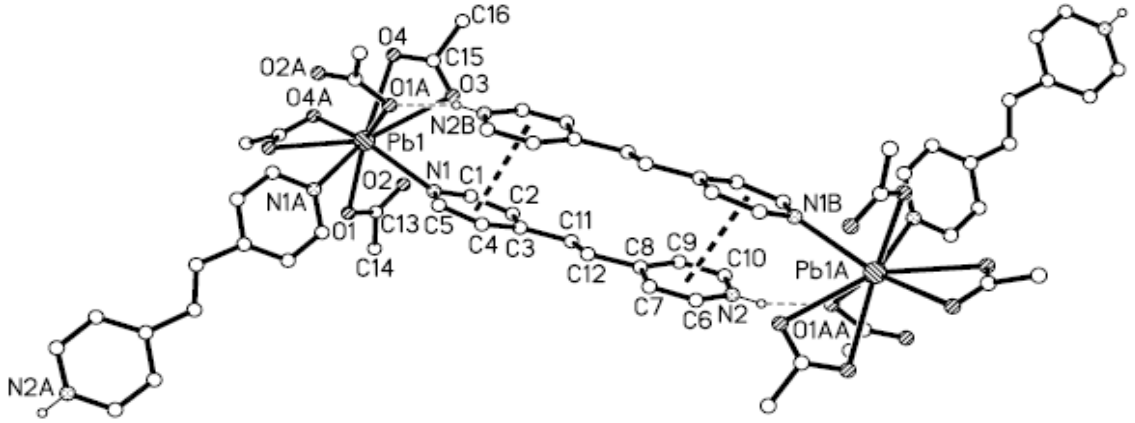


Figure ESI-2: A segment of the hydrogen bonded assembly showing the details of the supramolecular interactions and atom labeling scheme. Hydrogen bond parameters: N2-H2, 0.86 Å, N2···O1 (x-½, ½-y, z+½), 1.88 Å and N2-H2···O1, 165˚. The C-H hydrogen atoms and disordered atoms are not shown for clarity. The distance, 3.63 Å between the adjacent pyridyl groups in the chain indicates π···π interactions.

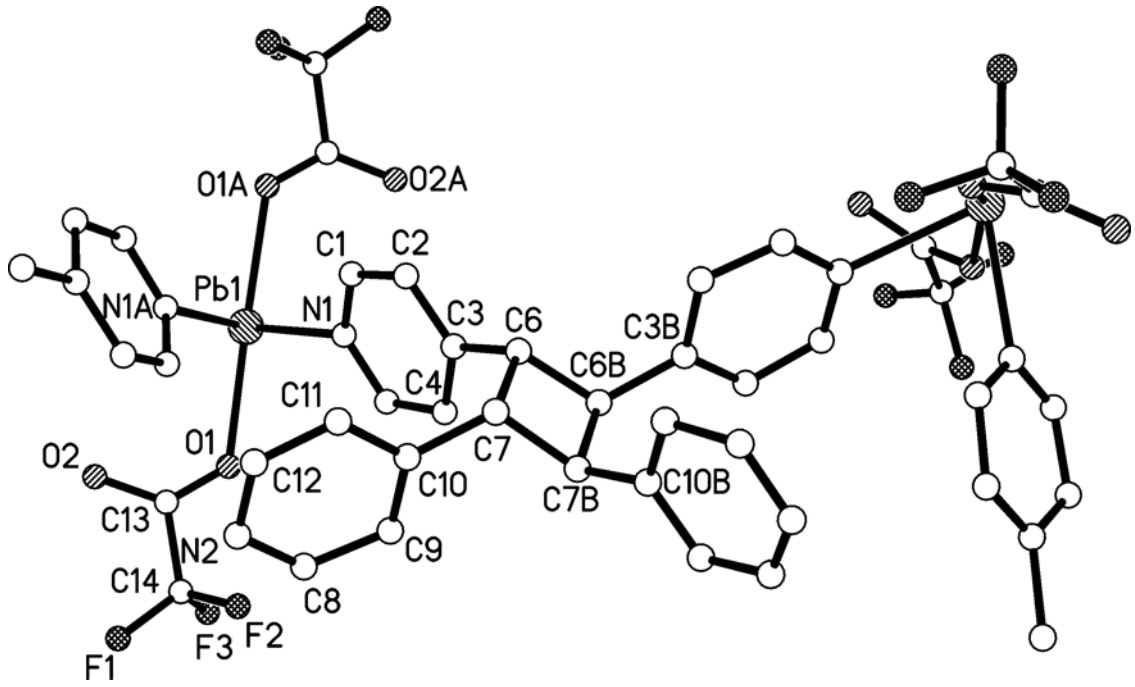


Figure ESI-3: A perspective view of the portion of **2a** showing the numbering scheme and geometry at the Pb(II) ions. The C-H hydrogen atoms and disordered F atoms are not shown for clarity. Presence of lone pair at the Pb(II) is indicated by large deviation of ideal angles for the trigonal bipyramidal shape for N1-Pb(1)-N1(z+3/4, -y+7/4, x-3/4) angle (73.3(4)˚) and O1-Pb-O1(z+3/4, -y+7/4, x-3/4) angle, (159.2(6)˚).

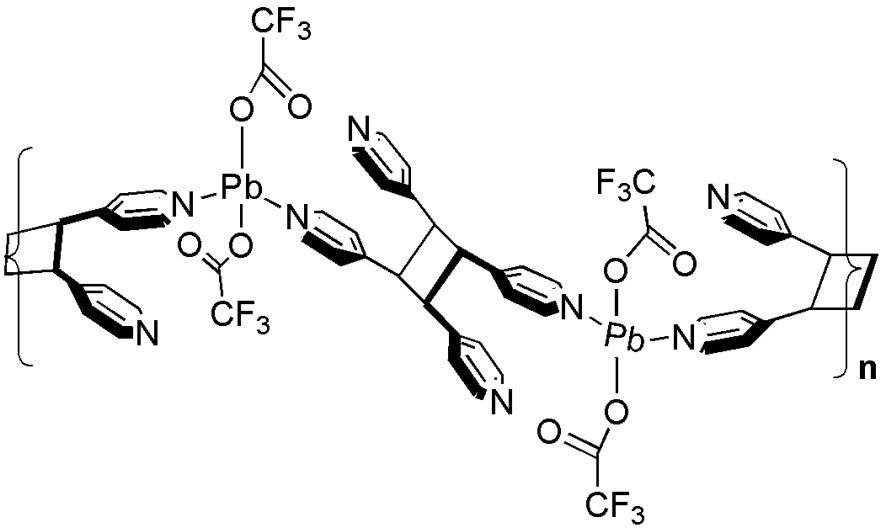


Figure ESI-4. A schematic diagram showing the expected connectivity of the photodimerized product from **1**. The stereochemistry of the cyclobutane product represents *rctt*-tpcb isomer.

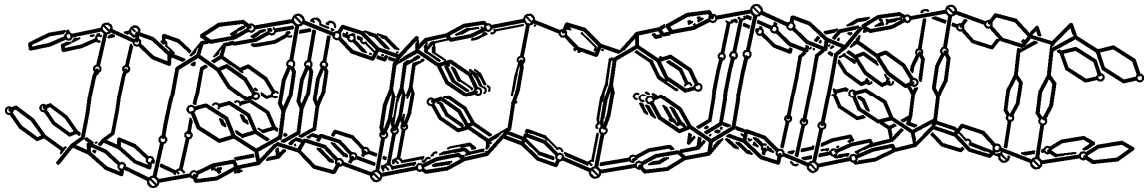
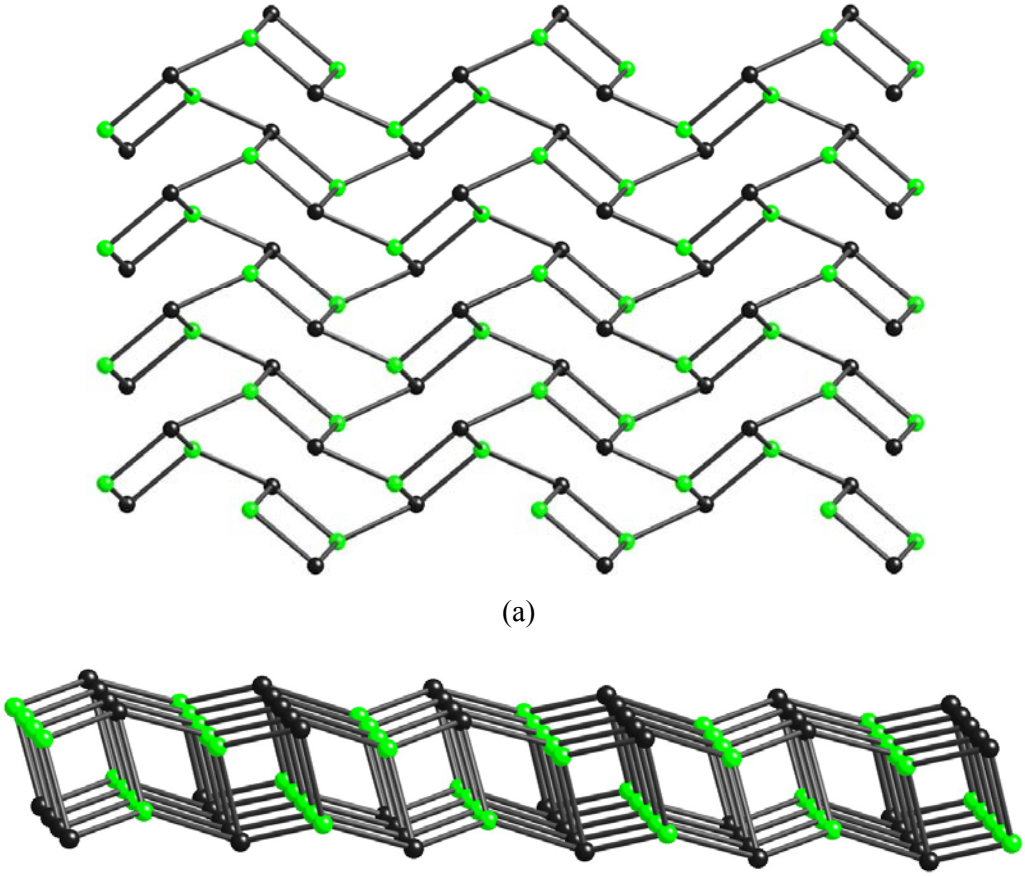


Figure ESI-5: A view of **3** from *b*-axis. The hydrogen atoms were omitted for clarity and $CF_3CO_2^-$ anions are not shown.

Crystal structure **3**: The squares are laid upright such that the Pb(II) and the pyridyl rings from the neighboring squares are connected to produce zigzag structure. The bottom edges of the squares are bonded to the adjacent rows alternately to form this 2D coordination polymeric sheet with the layer thickness of 8.7 Å (distance between Pb1 and C24). This connectivity generates larger ring linked by the edges of four squares which are parallel to the *b*-axis and empty spaces are occupied by the free non-bonded pyridyl rings of the *rcct*-tpcb ligands. The overall connectivity can be described as zigzag folded origami made from a sheet as shown in Figure ESI-5 below.



(a)

(b)

Figure ESI-6: Simplified schematic diagram showing the structure of **3** (a) in (101) plane and (b) viewed from *b*-axis. The black spheres at the T-joints represent Pb(II) atoms and the green spheres at the pyramidal joints represent tpcb ligands.

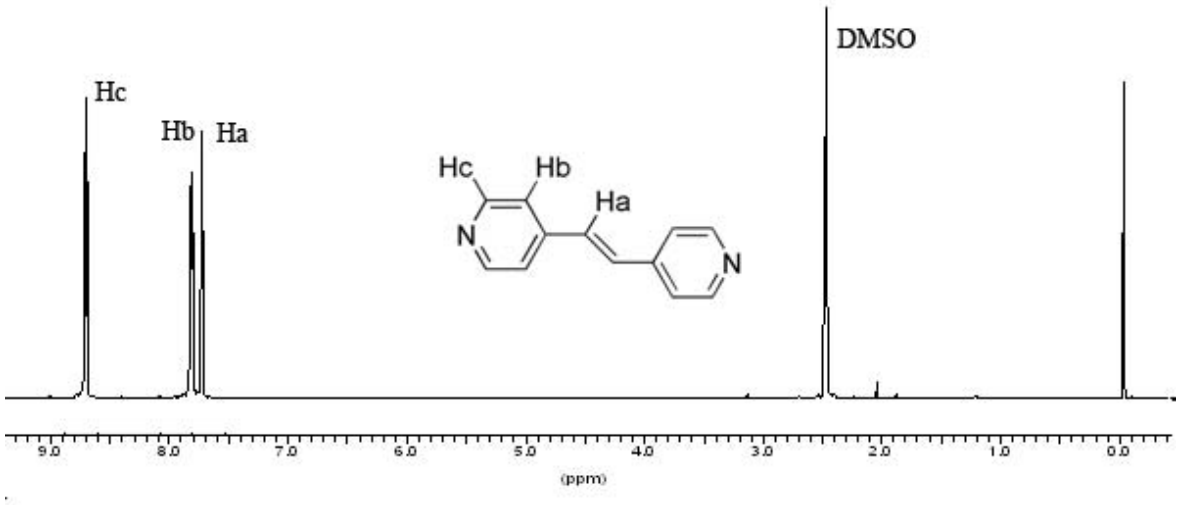


Figure ESI-7: ^{1}H NMR spectrum of **1** in D_6-DMSO (Zwitter ionic lead(II) complex before UV irradiation).

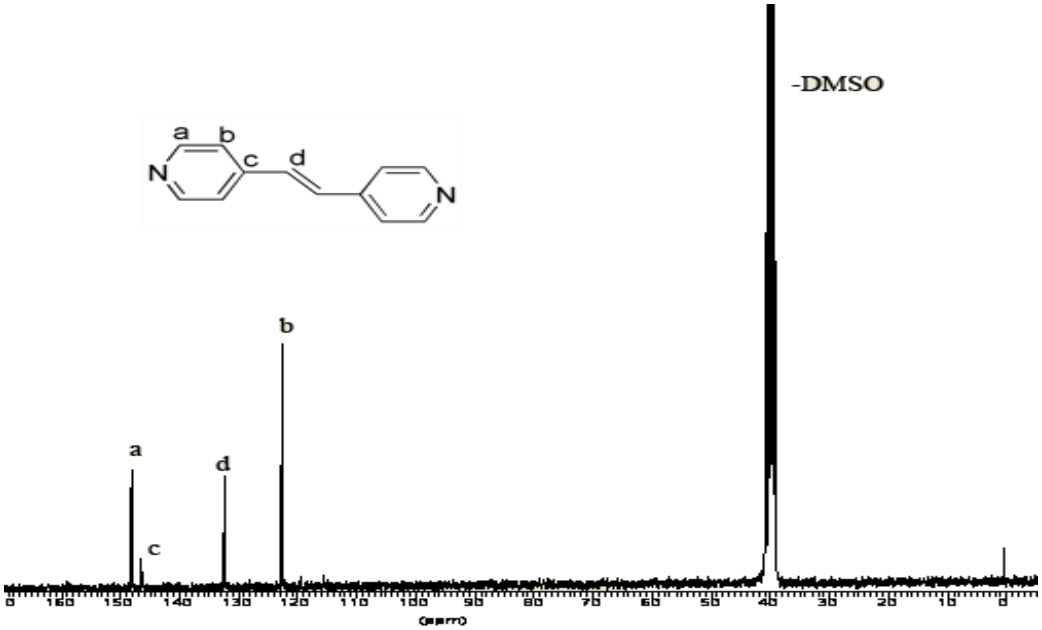


Figure ESI-8: ^{13}C NMR spectrum of **1** in D_6-DMSO (Zwitter ionic lead(II) complex before UV irradiation).

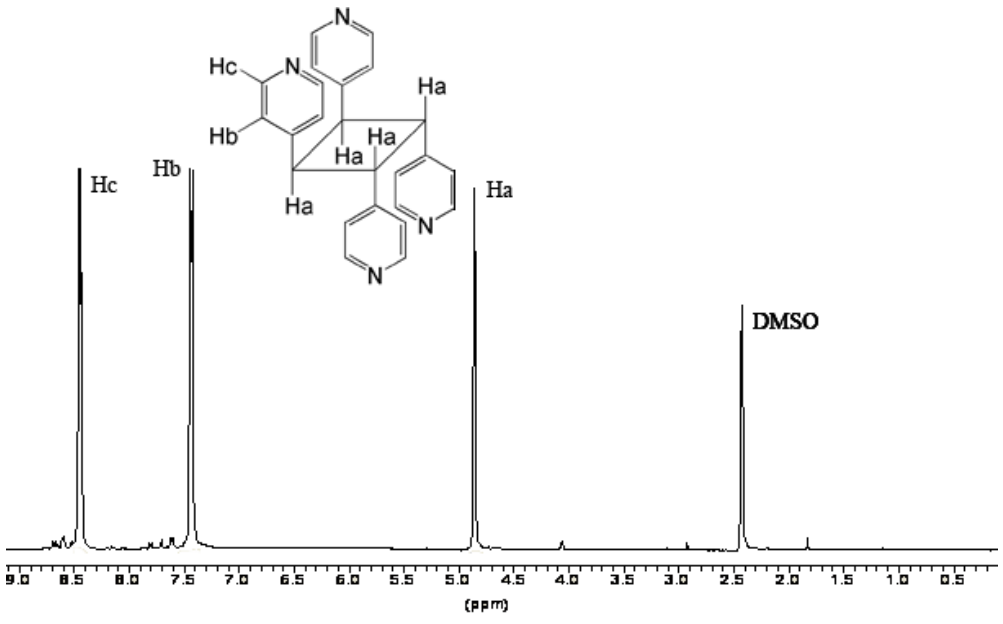


Figure ESI-9: ^{1}H NMR spectrum of **2** in D_6-DMSO (Zwitter ionic lead(II) complex after UV irradiation).

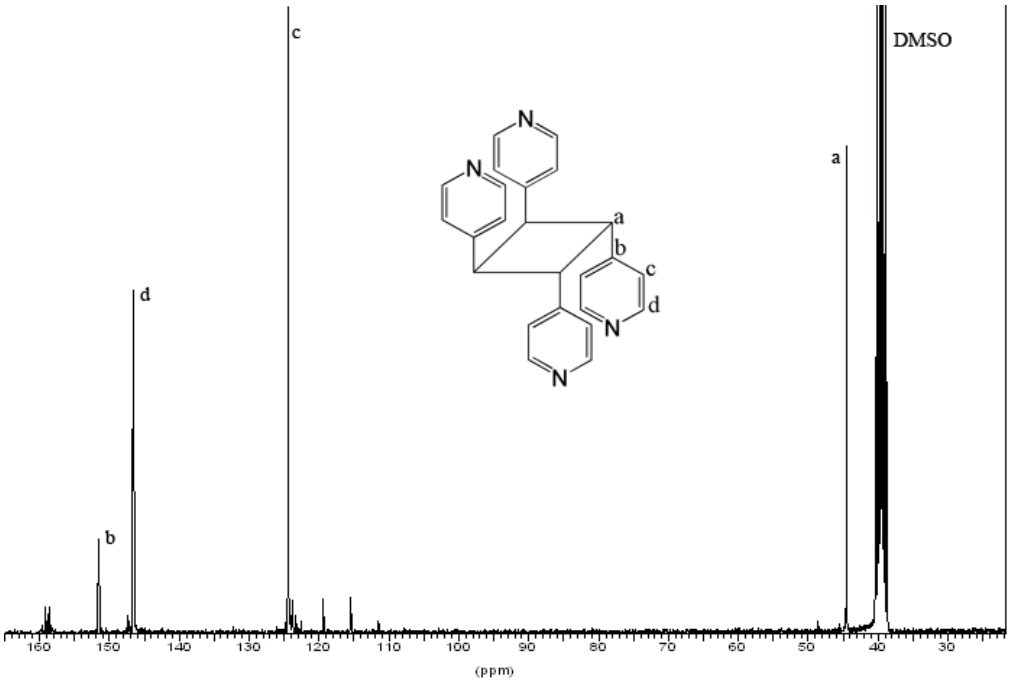


Figure ESI-10: ^{13}C NMR spectrum of **2** (Zwitter ionic lead(II) complex after UV irradiation).

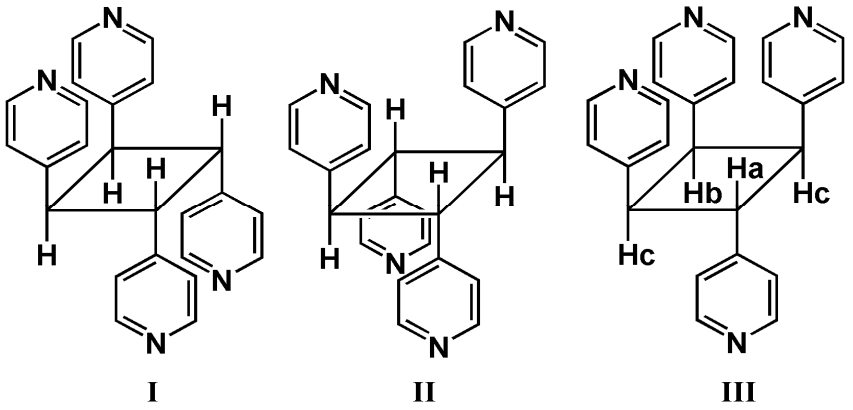


Figure ESI-11: 1, 2, 3, 4-tetrakis (4-pyridyl) cylobutane isomers(*rctt*-**I**, *rtct*-**II**, *rcct*-**II**)

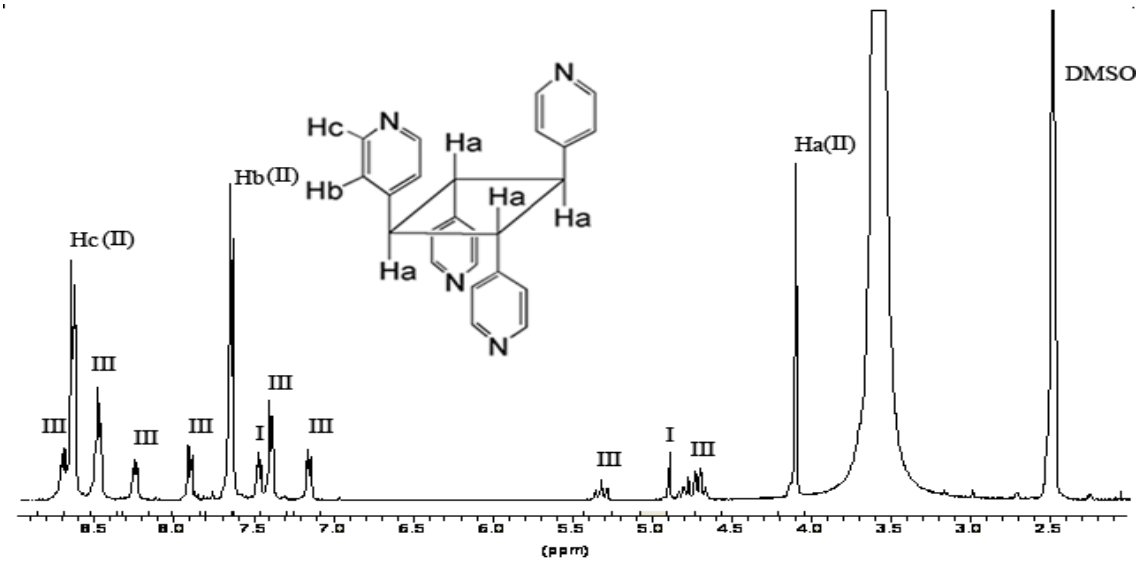


Figure ESI-12: The ^{1}H NMR spectrum of the white solid obtained by evaporating a methanolic solution of **2** after 4 days. The ^{1}H NMR spectra indicates the Pb(II) complexes with the isomers *rctt*: *rtct*: *rcct* (**I** : **II** : **III**)are in the ratio 5:47:48 ratio by integration.

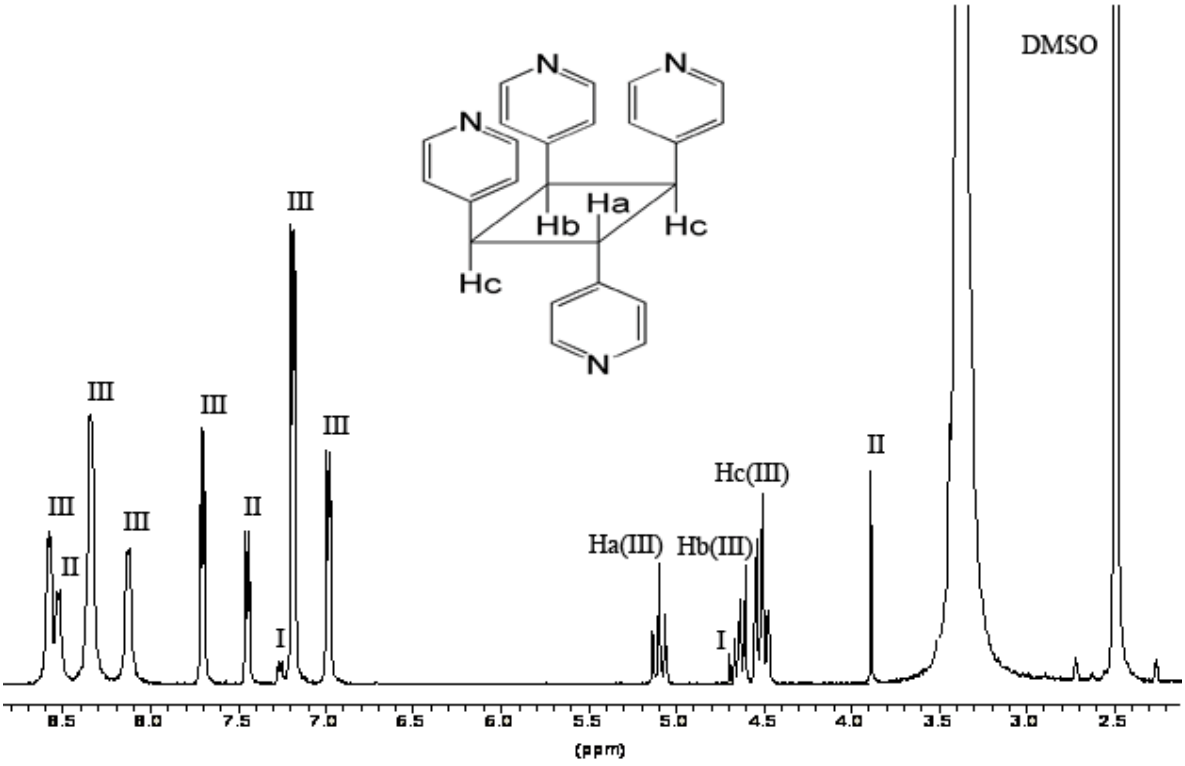


Figure ESI-13: The ^{1}H NMR spectrum of white solid **2** in D_6-DMSO. The white solid of **2** was obtained by evaporating solution mixture of **2** in MeOH/Ether. The ratio of Pb(II) complex with isomers *rtct*: *rcct* (**II**: **III**)= 12: 88 by integration.

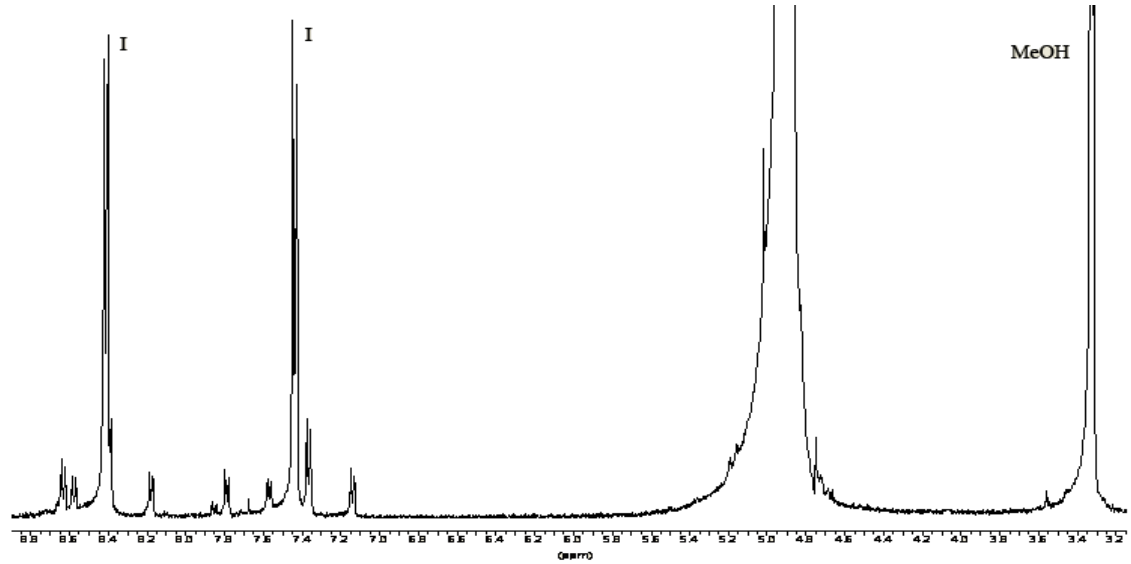


Figure ESI-14: ^{1}H NMR spectrum of **2** in CD_3OD recorded after two days. The ^{1}H NMR spectra indicates the gradual isomerisation of *rctt*-tpcb isomer to *rcct*-tpcb and *rtct*-tpcb.

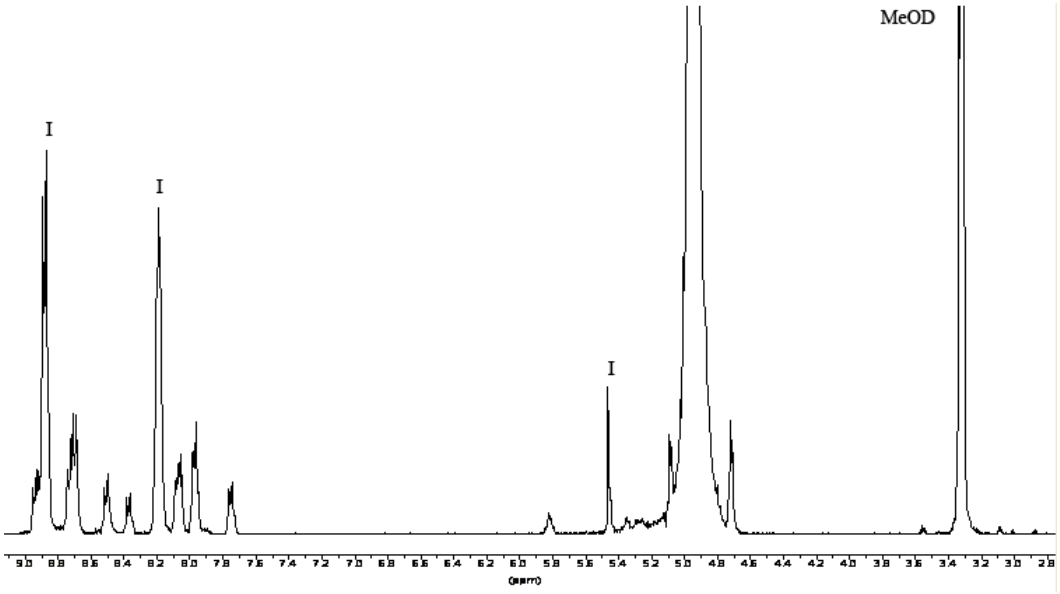


Figure ESI-15: ^{1}H NMR spectrum of **2** in CD_3OD after addition of TFA. The spectra indicate the increase in isomerization after two days.

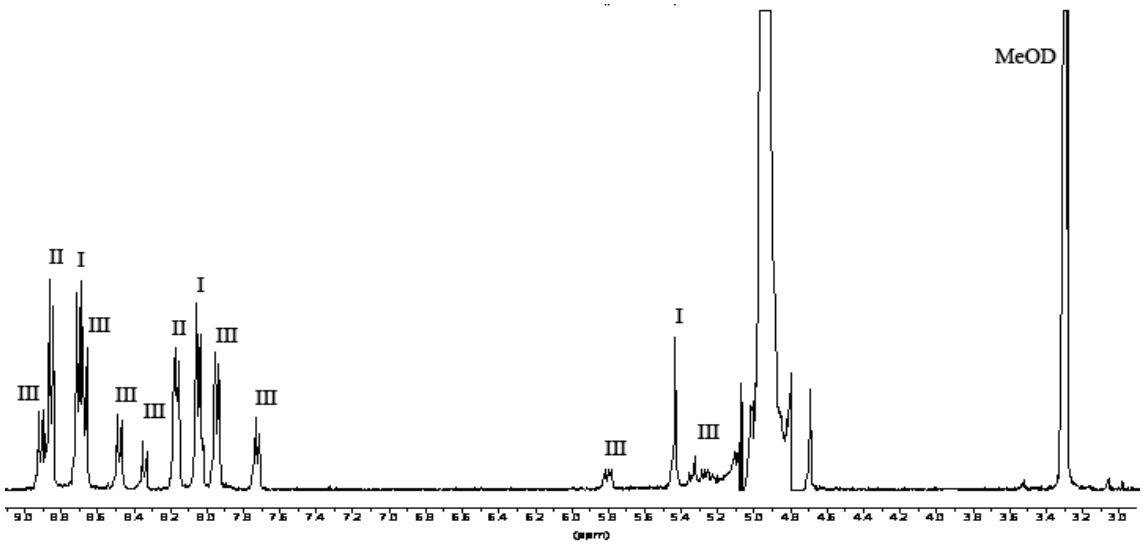


Figure ESI-16: ^{1}H NMR spectrum of **2** in CD_3OD after addition of TFA .The spectrum recorded after three days.

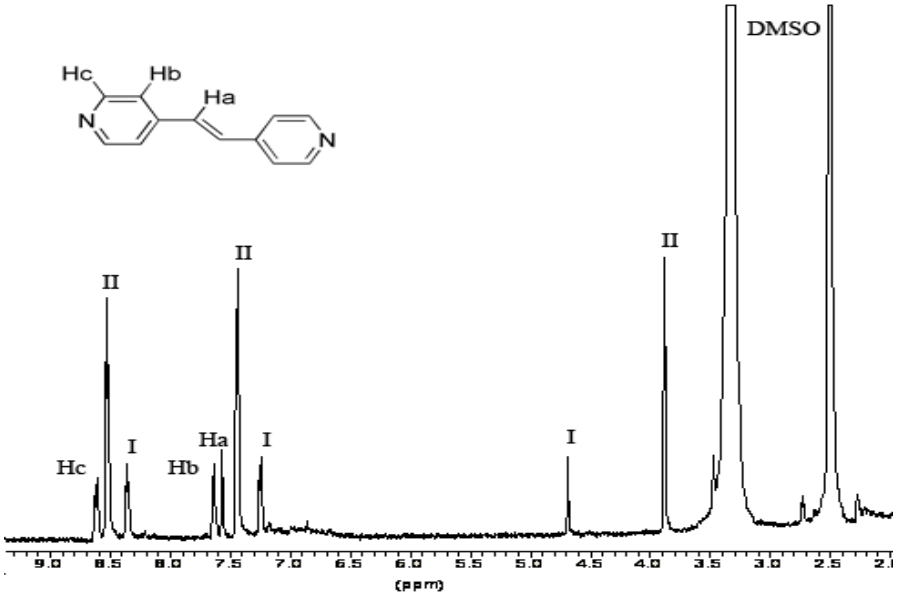


Figure ESI-17: When attempted to grow single crystals from CH_3CN solution, white solid was precipitated after five days. The ^{1}H NMR spectrum of this white solid dissolved in D_6-DMSO surprisingly shows the presence of bpe along with isomer *rtct*(**II**). X-ray structure determination of a single crystal separated from this solid mixture confirmed that it is the lead(II) complex, **1** which accounts for the observed signals from bpe in the ^{1}H NMR spectrum discussed above.

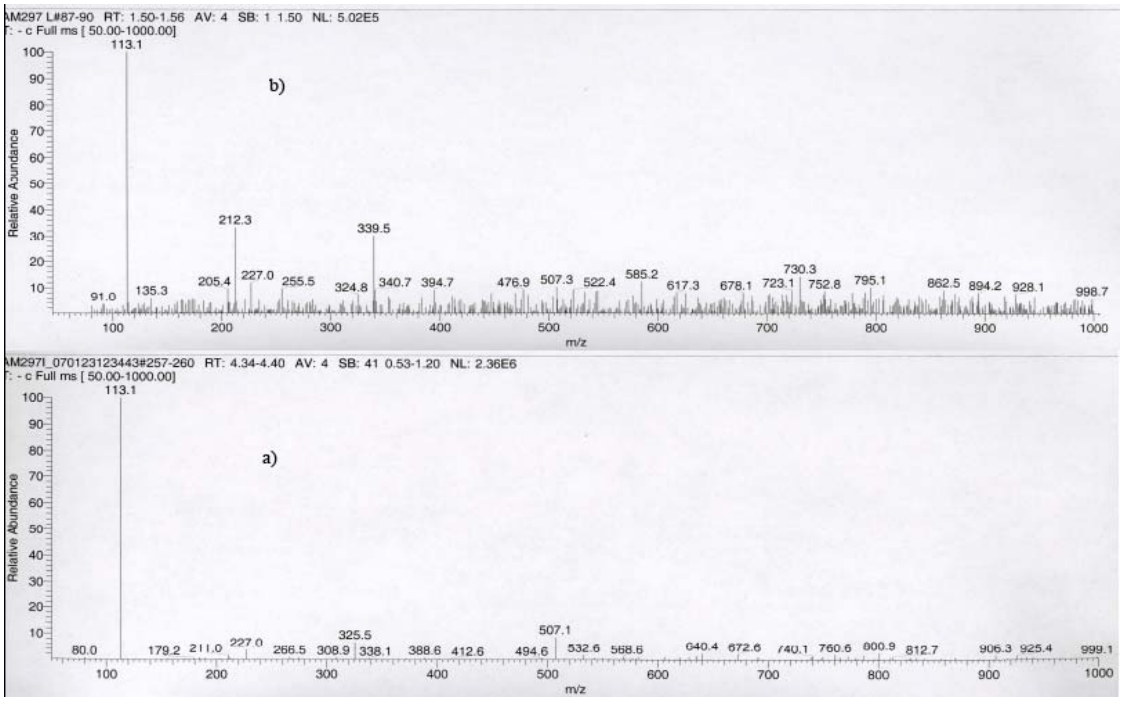


Figure ESI-18: ESI$^-$ MS of **2** showing the presence of CF_3CO_2H. (m/z), (%): 113.1(100) [M$^-$-H]. (a) ESI$^-$ MS of standard CF_3COOH in toluene. (b) CF_3COOH collected and distilled from the irradiated product **2** in toluene