Supporting information

Dinuclear uranium(VI) salen coordination compound: An efficient visible light active catalyst for selective reduction of CO_2 to methanol

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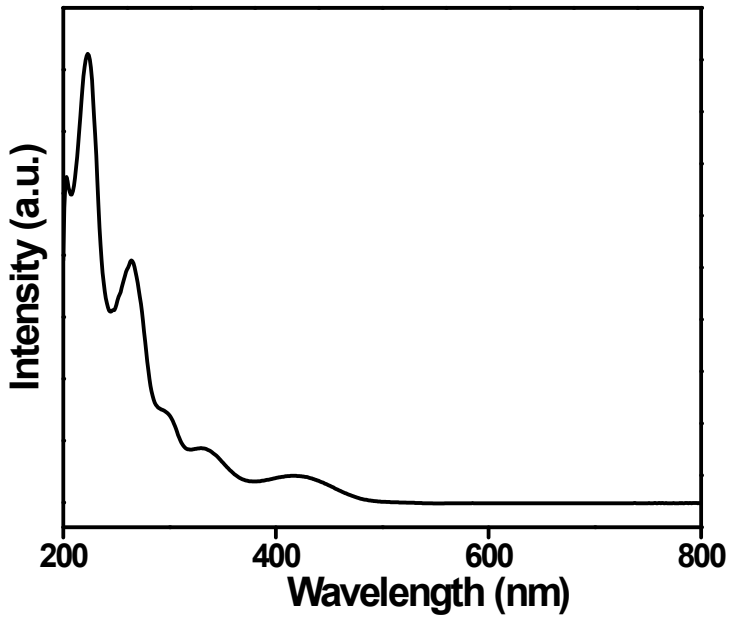


Fig. S1 UV-vis absorption spectrum of [(UO2)2(L)2].2MeCN in MeCN

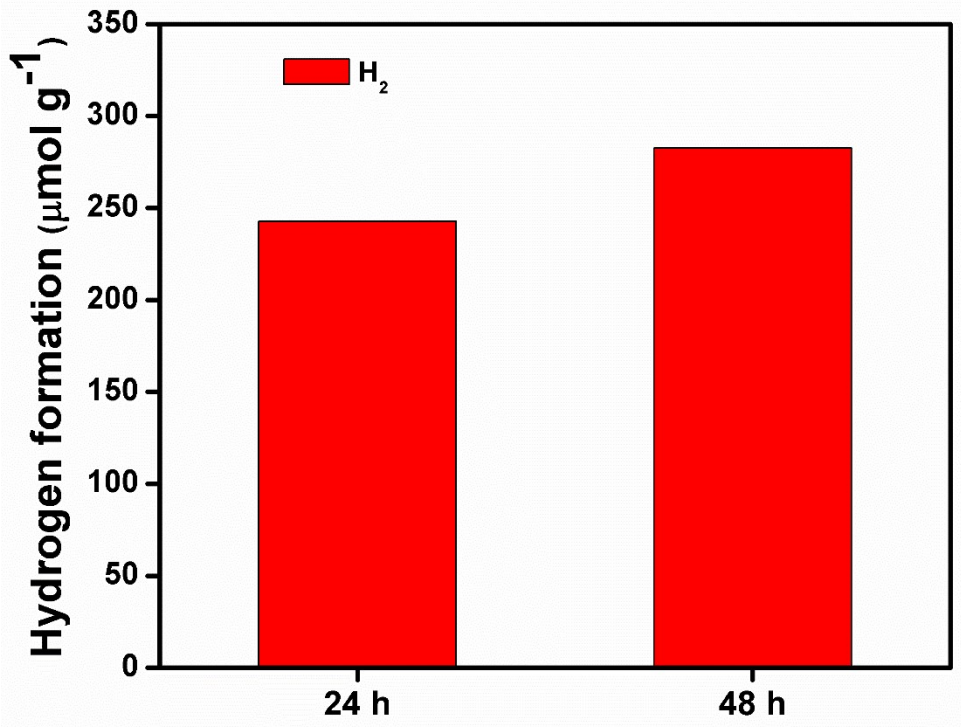


Fig. S2 The formation of H_2 from MeCN: H_2O: TEOA mixture under visible light during the photocatalytic reduction of CO_2.

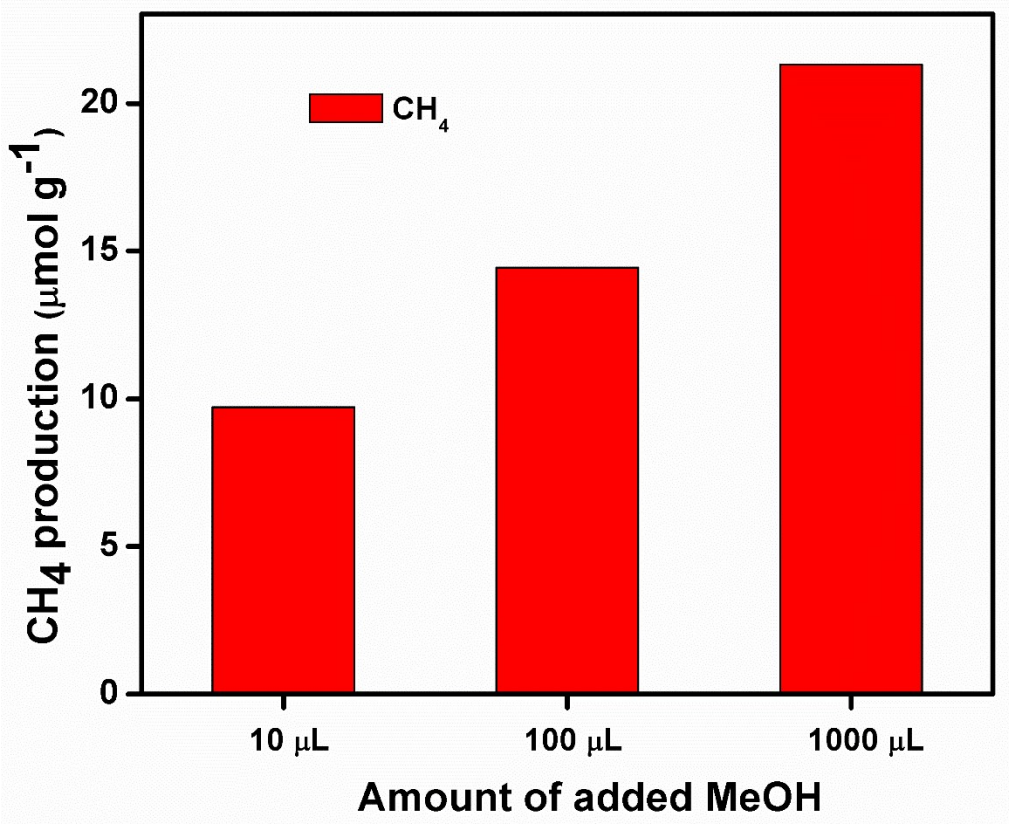


Fig. S3 The formation of CH_4 from MeCN:H_2O:TEOA mixture in the presence of different concentrations of MeOH

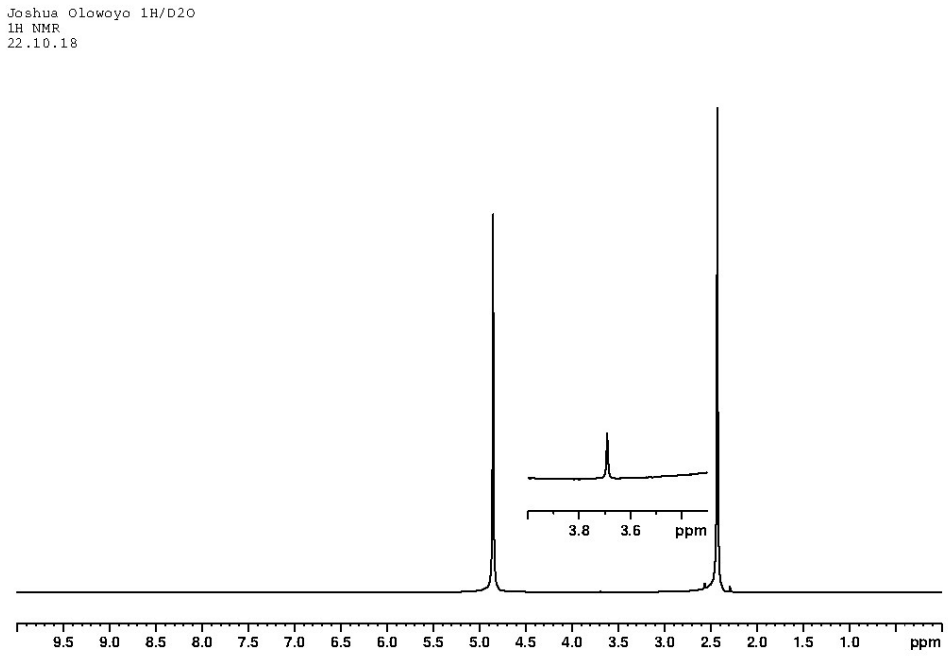


Fig. S4 ^{1}H NMR spectrum of the photocatalytic product from the reduction of $^{13}CO_2$.

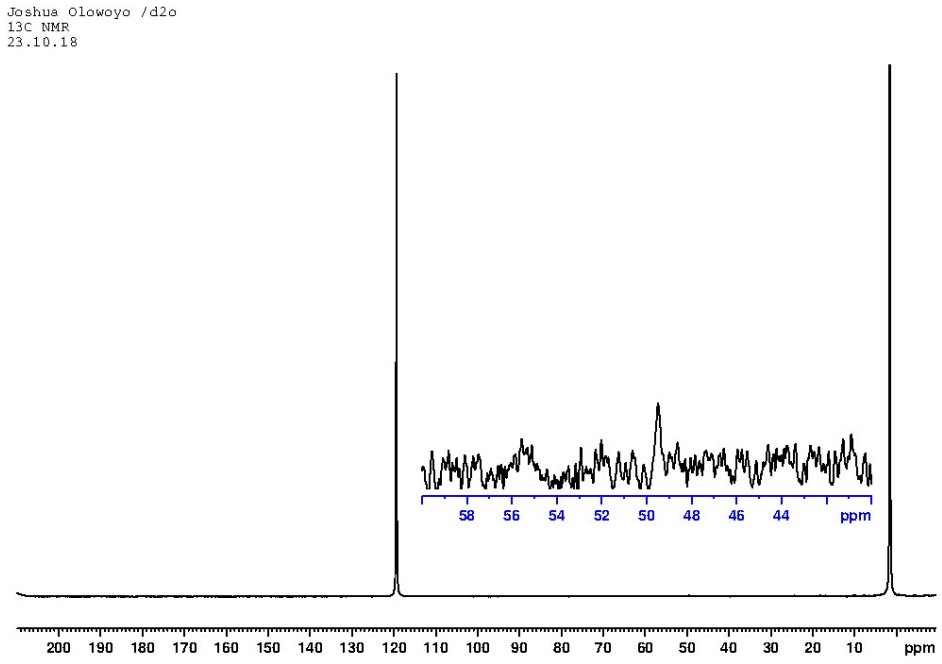


Fig. S5 ^{13}C NMR spectrum of the photocatalytic product from the reduction of $^{13}CO_2$

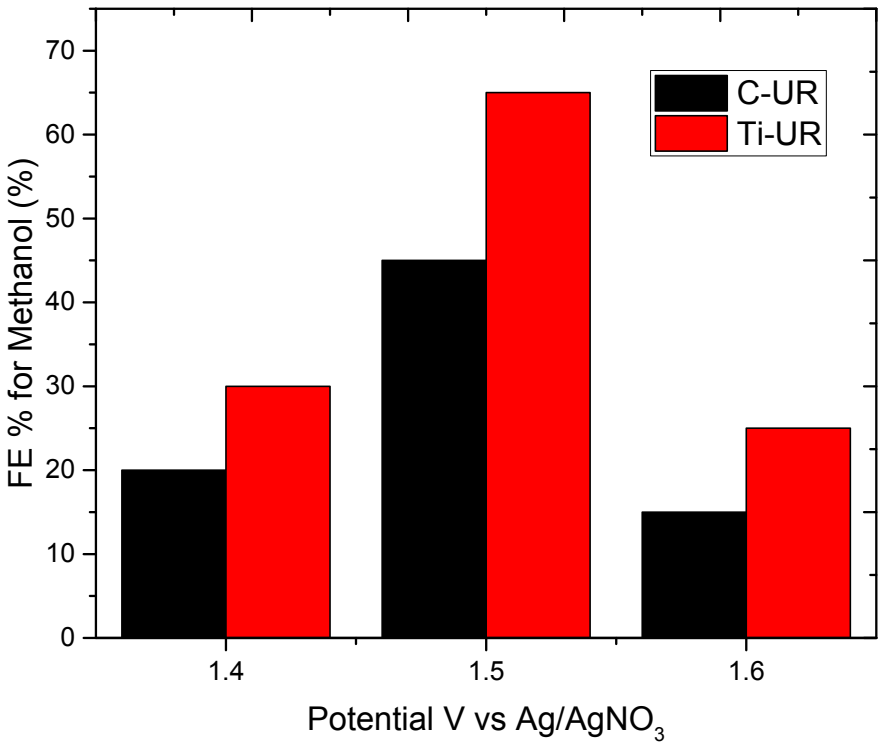


Fig. S6 Faradaic efficiency of MeOH production for two different electrodes of GDL with the catalyst (C-UR) and Ti compound (Ti-UR) in the solution of 0.1M Bu_4NPF_6 in MeCN being bubbled with CO_2 in 3 different potentials after 2 hours of test

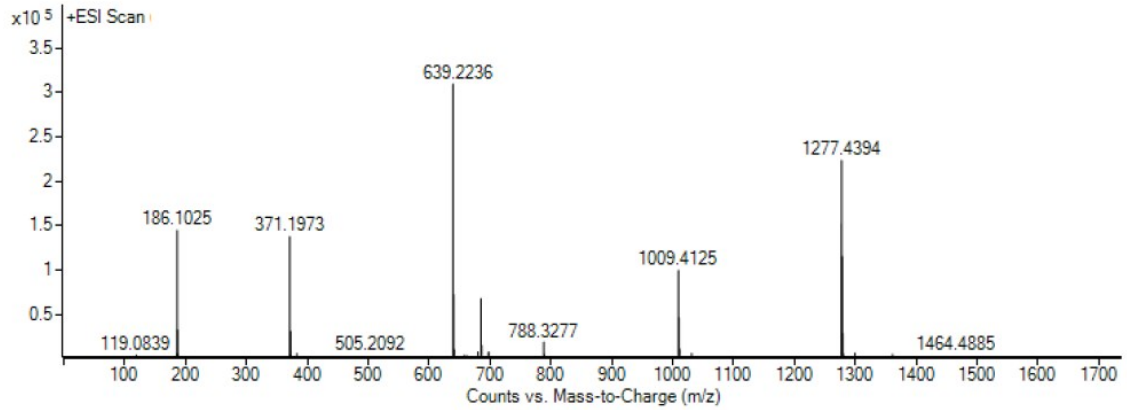


Fig. S7 ESI mass spectrum of the title complex in MeCN

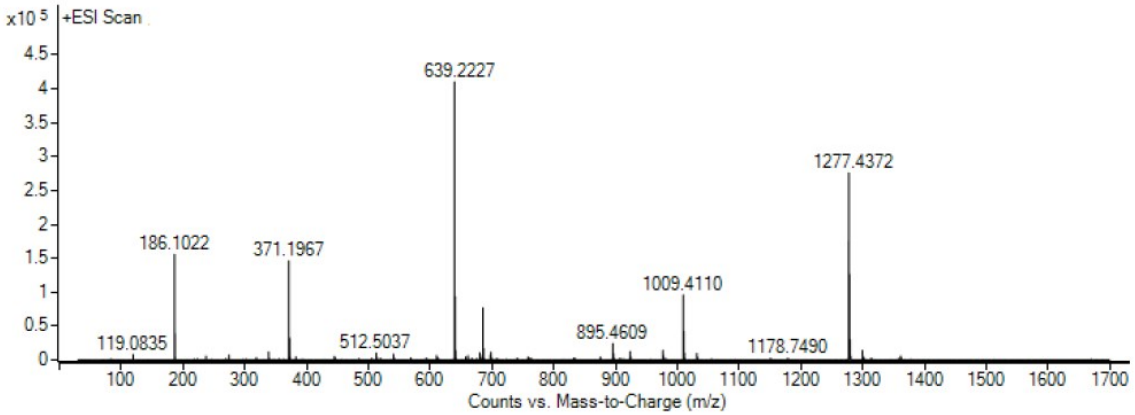


Fig. S8 ESI mass spectrum of the title complex before the photocatalytic reduction of CO_2 in the MeCN: H_2O: TEOA

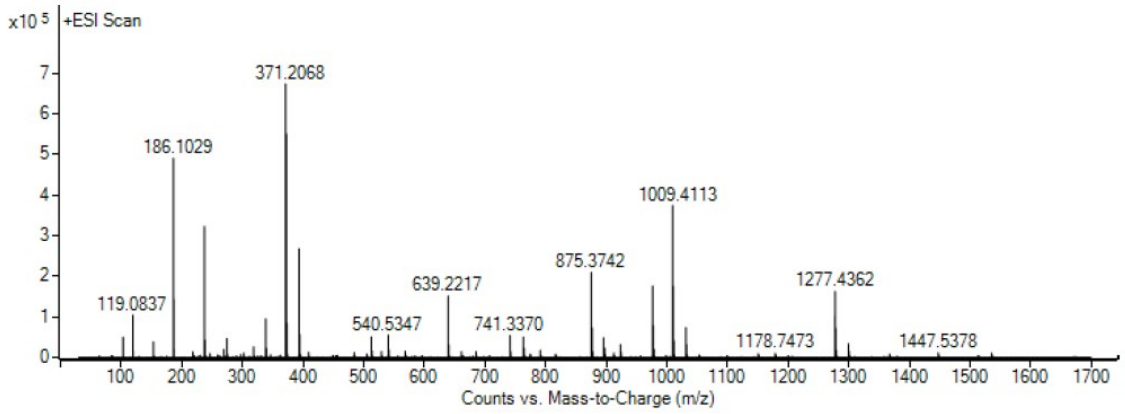
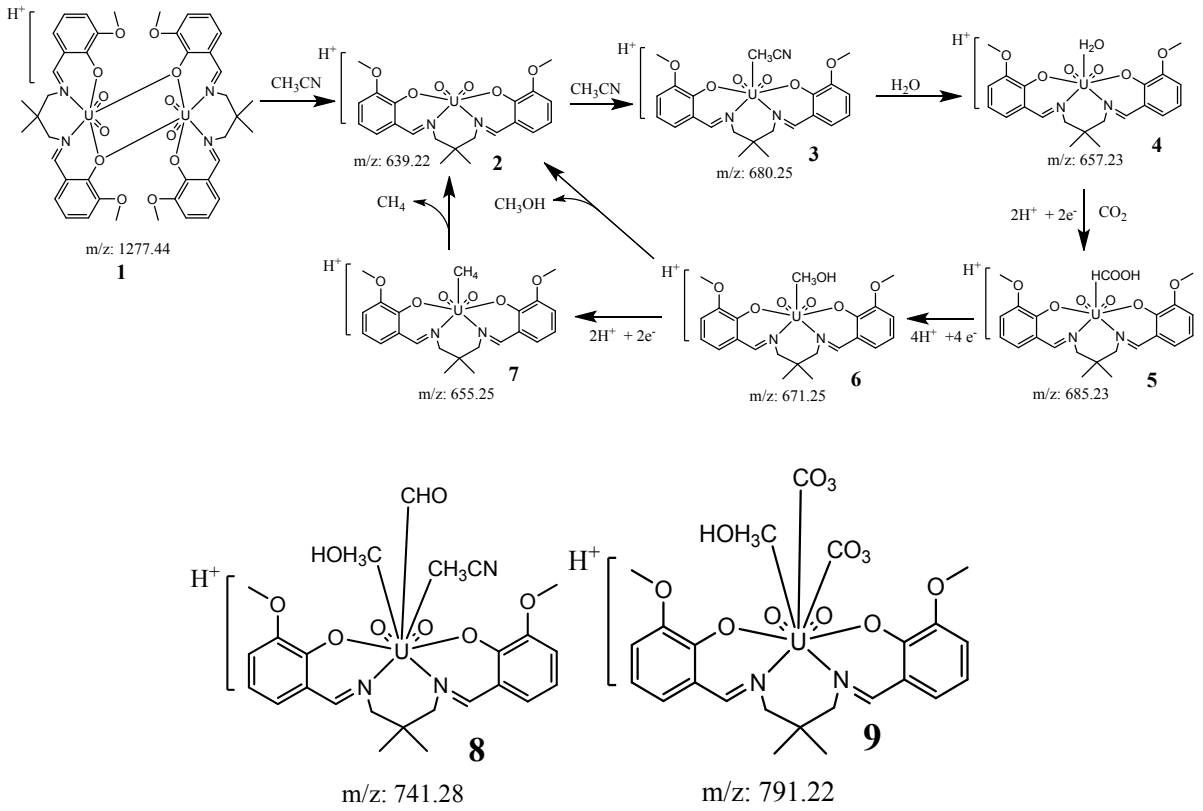


Fig. S9 ESI mass spectrum of the title complex after the photocatalytic reduction of CO_2 in MeCN:H_2O:TEOA under visible light irradiation.



Scheme S1 Possible structures of the catalyst on interaction with reactant, product and intermediate products on photocatalytic reduction of CO_2 under visible light.

The ^{1}H NMR spectrum of the title complex contains two sets of resonant frequencies originating from aliphatic and aromatic protons. A sharp singlet of azomethine (4H, -CH=N) resonance exists at 8.31 ppm and of $–OCH_3$, $-CH_2$ and $–CH_3$ protons appear at 3.90 ppm, 3.48 ppm, and 1.05 ppm, respectively. The broad peaks at 6.79-6.99 ppm reflect the resonant frequencies of aromatic protons [Fig. S10].

The ^{13}C NMR spectrum of the title complex contains peaks at 24.2 ppm, 56.0 ppm, 67.3 ppm, 36.1 ppm, associated with $–CH_3$, quaternary carbon atom, $-CH_2$ and $–OCH_3$ resonant frequencies, respectively. The most characteristic signal of the spectrum, originating from the presence of an azomethine functional group, appears at 165.7 ppm. The resonant frequencies generated by the Ar-**C**-O- and Ar-**C**-O-CH_3 carbon atoms are at 152.0 ppm, and 148.4 ppm, respectively. The signals at 113.7-122.8 ppm are assigned to aromatic carbon atoms [Fig. S11].

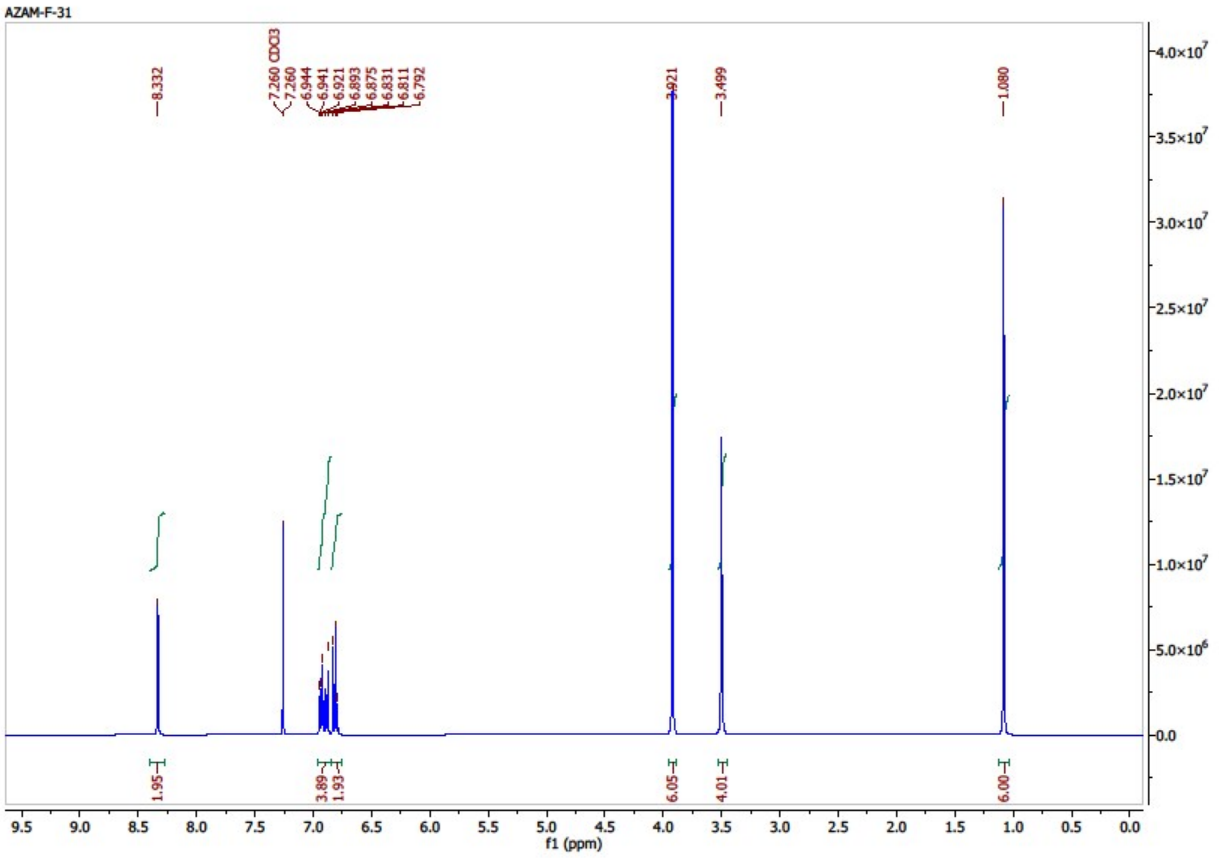


Fig. S10. ^{1}H NMR spectrum of the title complex

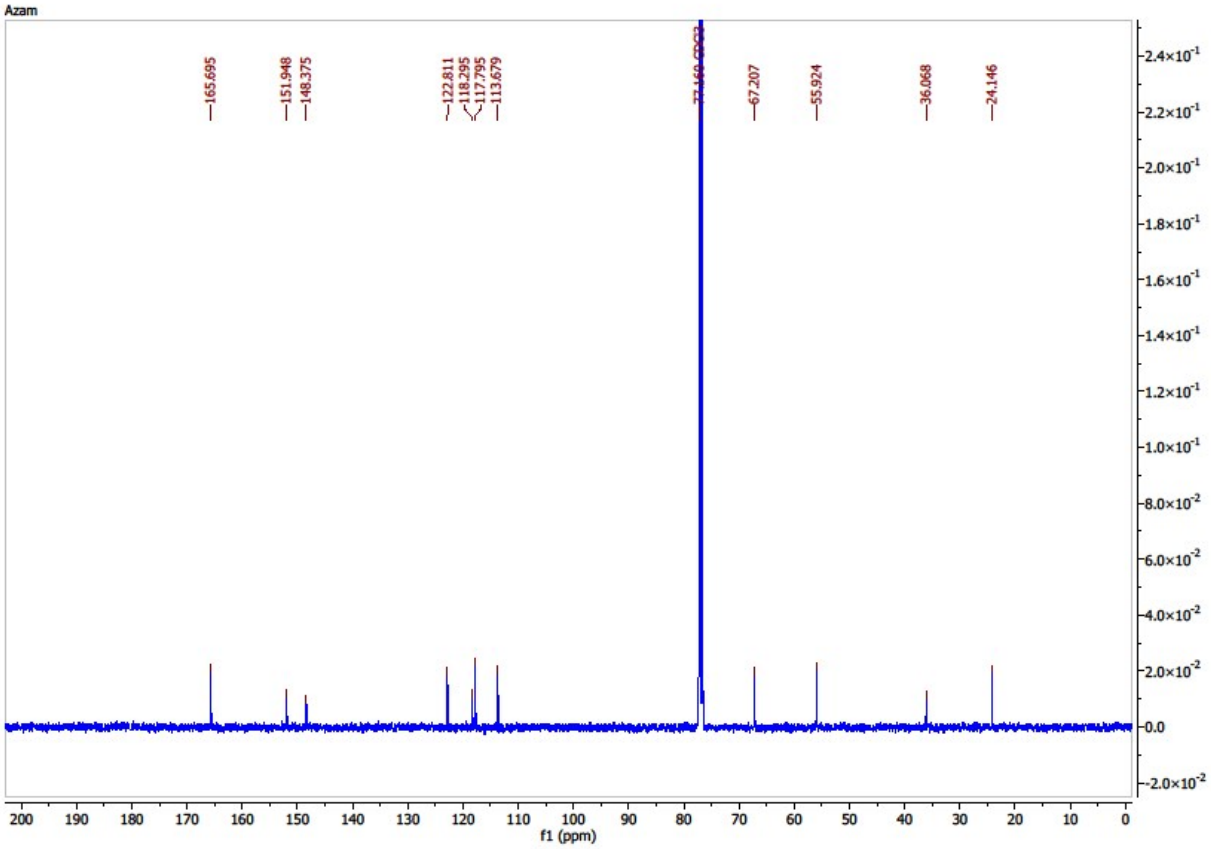


Fig. S11. ^{13}C NMR spectrum of the title complex

The IR spectrum possesses well-shaped band at 1592 cm^{-1} caused by $\upsilon_{(-CH=N)}$ vibrations. This also confirms the presence of an azomethine group in the studied compound[1]. The most characteristic band of the coordinated uranyl ion exists at 987 cm^{-1}, and this value is typical for uranium in a similar environment[2-3]

References

1. N. E. El-Gamel, *RSC adv.,* 2012, **2**, 5870-5876.

2. R. Kannappan, S. Tanase, D. M. Tooke, A. L. Spek, I. Mutikainen, U. Turpeinen and J. Reedijk, *Polyhedron*, 2004, **23**, 2285-2291.

3. G. A. Kolawole and K. S. Patel, *J. Chem. Soc., Dalton Trans.*, 1981, 1241-1245.

Table S1. Crystal and structure refinement data of the complex

Compound	**Compound**
Empirical formula	$C_{46}H_{54}N_6O_{12}U_2$
Formula weight	1359.01
Crystal system, space group	triclinic, *P*-1 (No. 2)
Unit cell dimensions [Å, °]	a = 8.95682(16)
	b = 14.2454(2)
	c = 18.8663(3)
	α = 82.0310(13)
	β = 84.2723(13)
	γ = 89.8078(14)
Volume [Å^3]	2371.93(7)
Z, Calculated density [Mg/m^3]	2, 1.903
F(000)	1304
Crystal size [mm]	0.168, 0.135, 0.080
θ range for data collection [°]	3.661 to 79.112
Index ranges	$-11 \le h \le 9$, $-18 \le k \le 15$, $-23 \le l \le 24$
Reflections collected / unique	39298 / 10051 [$R_{(int)}$ = 0.0326]
Completeness [%]	100% (to θ = 67°)
Data / restraints / parameters	10051 / 0 / 606
Goodness-of-fit on F^2	1.189
Final *R* indices [$I>2\sigma(I)$]	$R1$ = 0.0306, $wR2$ = 0.0884
R indices (all data)	$R1$ = 0.0306, $wR2$ = 0.0885
Largest diff. peak and hole [e•Å^{-3}]	1.982, -1.503

Table S2. Selected distances and angles of complex [Å].

Uranyl complex			
U1—O5	1.788(3)	U2—O11	1.776(3)
U1—O6	1.788(3)	U2—O12	1.786(3)
U1—O2	2.235(3)	U2—O8	2.249(3)
U1—O1	2.377(3)	U2—O1	2.513(3)
U1—O7	2.545(3)	U2—O7	2.377(3)
U1—N1	2.558(4)	U2—N3	2.533(4)
U1—N2	2.594(4)	U2—N4	2.587(4)
C7—N1	1.295(6)	C28—N3	1.291(6)
N1—C8	1.465(6)	N3—C29	1.477(6)
C12—N2	1.466(6)	C33—N4	1.474(6)
N2—C13	1.286(6)	N4—C34	1.293(6)
O5—U1—O6	170.12(14)	O11—U2—O12	168.08(15)
O5—U1—O2	90.41(14)	O11—U2—O8	89.60(14)
O6—U1—O2	93.16(13)	O12—U2—O8	94.97(14)
O5—U1—O1	95.28(13)	O11—U2—O7	94.60(13)
O6—U1—O1	86.04(13)	O12—U2—O7	87.13(13)
O2—U1—O1	150.96(11)	O8—U2—O7	149.13(11)
O5—U1—O7	80.55(12)	O11—U2—O1	78.67(13)
O6—U1—O7	108.74(12)	O12—U2—O1	112.60(13)
O2—U1—O7	88.28(11)	O8—U2—O1	85.74(11)
O1—U1—O7	64.77(10)	O7—U2—O1	65.29(10)
O5—U1—N1	84.01(13)	O11—U2—N3	82.14(14)
O6—U1—N1	87.31(13)	O12—U2—N3	87.40(13)
O2—U1—N1	139.59(12)	O8—U2—N3	140.88(12)
O1—U1—N1	69.42(11)	O7—U2—N3	69.92(11)
O7—U1—N1	129.66(11)	O1—U2—N3	129.12(11)
O5—U1—N2	88.63(13)	O11—U2—N4	88.37(14)
O6—U1—N2	83.91(13)	O12—U2—N4	82.80(13)
O2—U1—N2	70.38(11)	O8—U2—N4	70.61(12)
O1—U1—N2	138.05(11)	O7—U2—N4	139.96(12)
O7—U1—N2	156.05(11)	O1—U2—N4	153.15(11)
N1—U1—N2	69.50(11)	N3—U2—N4	70.99(12)
O5—U1—U2	76.00(10)	O11—U2—U1	74.28(11)
O6—U1—U2	109.77(10)	O12—U2—U1	112.78(11)
O2—U1—U2	120.93(8)	O8—U2—U1	118.08(9)
O1—U1—U2	35.15(7)	O7—U2—U1	35.96(8)
O7—U1—U2	33.26(7)	O1—U2—U1	33.00(7)
N1—U1—U2	96.49(8)	N3—U2—U1	96.39(8)
N2—U1—U2	160.43(8)	N4—U2—U1	160.02(8)

Table S3. Hydrogen bonds geometry of uranyl complex [Å, °].

D—H•••A	d(D-H)	d(H•••A)	<(DHA)	d(D•••A)
C20—H20C•••O12	0.96	2.58	3.099(7)	113.9
C42—H42B•••O8	0.96	2.57	3.137(6)	117.6
C52—H52C•••O4	0.96	2.50	3.203(8)	129.7
C62—H62C•••O6[x-1, y, z]	0.96	2.55	3.462(7)	159.2