Supporting Information
For

Crystal structure, DNA crosslinking and photo-induced cytotoxicity of oxovanadium(IV) conjugates of boron-dipyrromethene

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Computational methodology

To rationalize the photophysical properties of the complexes, computational studies were performed for both the complexes using B3LYP/LANL2DZ level of DFT.[S1] The hybrid B3LYP functional and LANL2DZ basis set were used in all calculations as incorporated in Gaussian 09 package.[S2] Visualizations of the optimized structures and the MOs were performed using Chemcraft 1.7. To ascertain stationary points, further frequency test was performed.

References

(S1) (a) A. D. Becke, *Phys. Rev*., 1998, **A38**, 3098-3100; (b) A.D. Becke, *J. Chem. Phys*., 1993, **98**, 5648-5652; (c) C. Lee, W. Yang and R.G. Parr, *Phys. Rev., B*. 1988, **37**, 785-789; (d) P.J. Hay and W.R. Wadt, *J. Chem. Phys*., 1985, **82**, 284-298.

(S2) Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H.Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L.Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T.Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F.Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi,J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi,N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo,R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W.Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J.Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J.Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
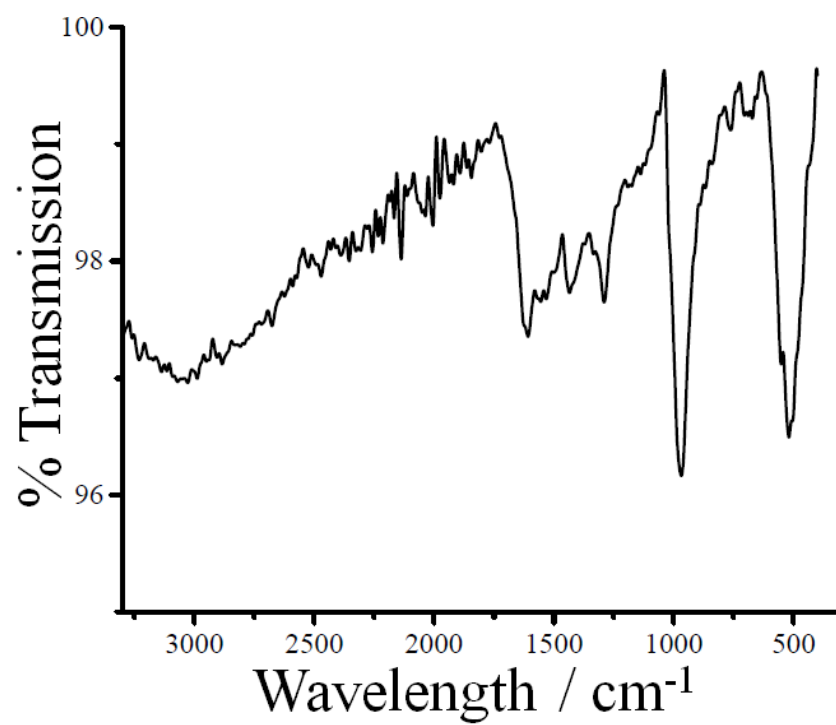
Fig S1. IR spectrum of complex **3**
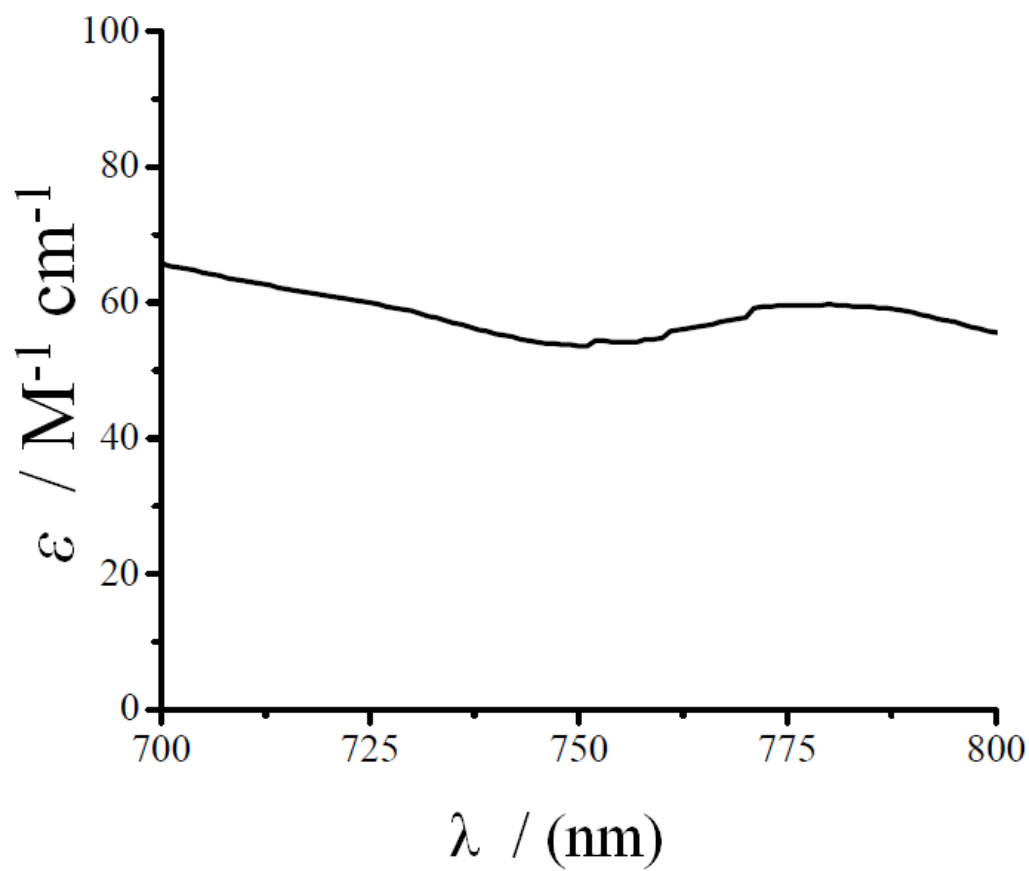
Fig S2. Absorption spectrum of the complex 2, showing the weuous DMF.
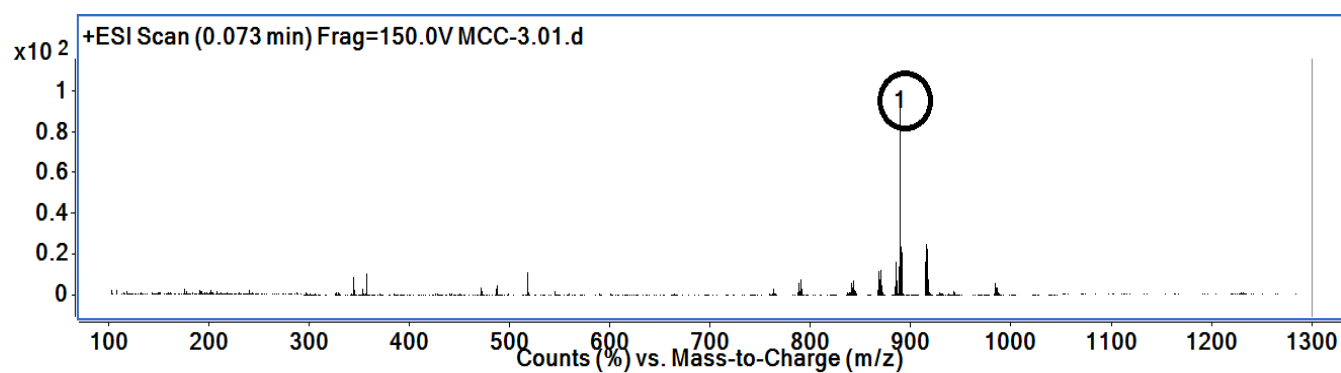
Fig S3. The ESI-mass spectrum of complex **3** showing the prominent $[M-Cl]^+$ (889.0956) peak in methanol
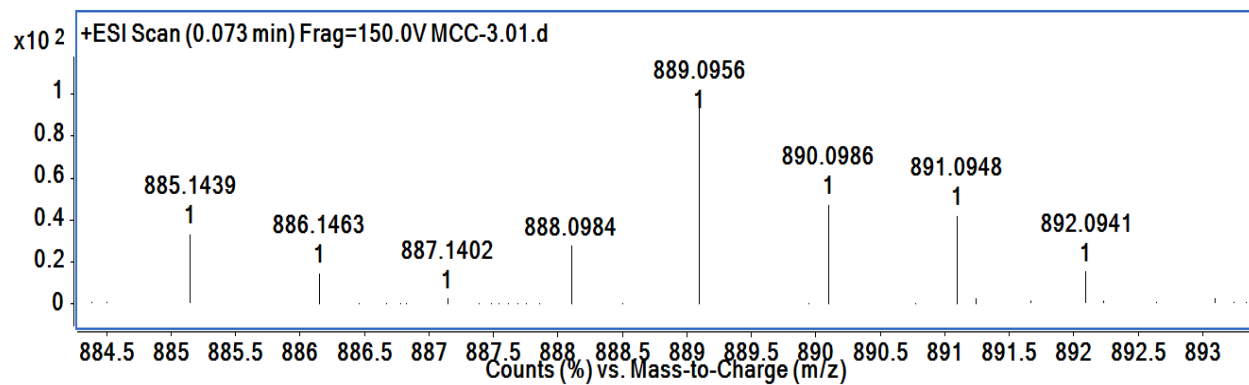
Fig S4. The isotopic distribution of the molecular ion peak.
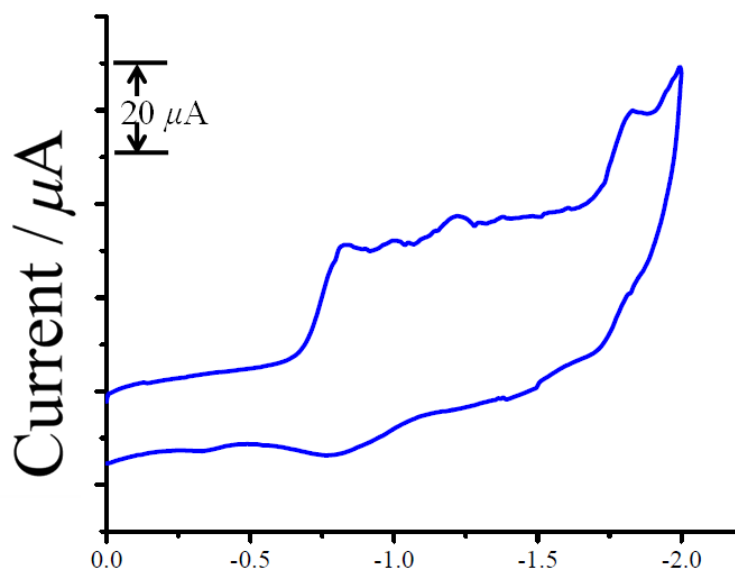
Fig S5. Cyclic voltammograms of the complex **3** showing the cathodic response in DMF at a scan rate of 50 mV s^{-1} and 0.1 mol TBAP as the supporting electrolyte.
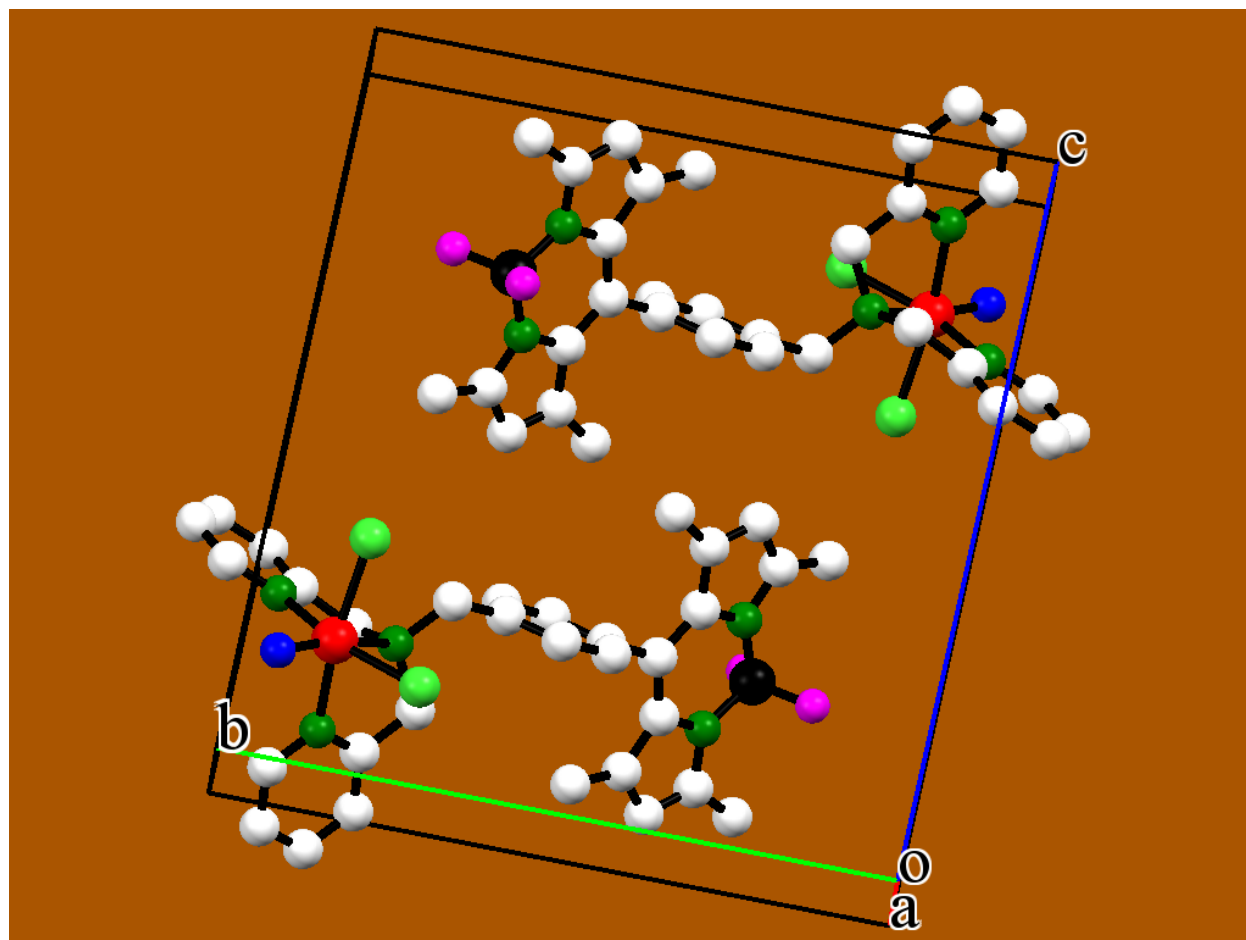
Fig. S6. Unit cell packing diagram of complex **1** [color codes: C white, N green, O blue, V red, Cl light green, B Black, F pink].
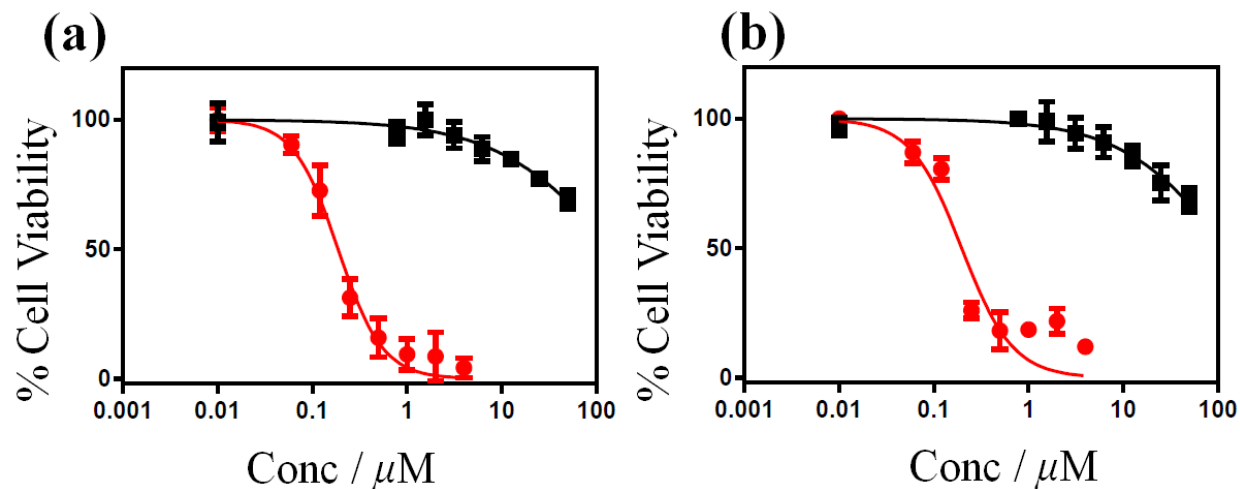
Fig. S7. Photocytotoxicity of the complex **3** in (a) HeLa cell lines (b) MCF-7 cell lines on 4 h incubation in dark followed upon photo-irradiation in visible light (400 to 700 nm) for 1 h as determined by MTT assay. The photo-exposed and dark-treated cells are shown in red and black colour symbols, respectively.
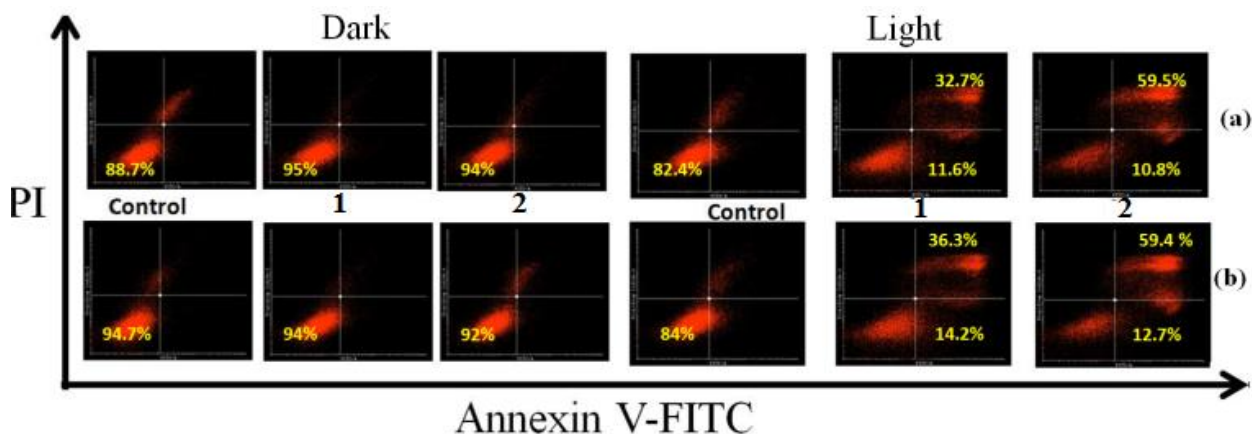
Fig. S8. FACScan profiles of Annexin-V FITC and propidium iodide (PI) staining of (a) HeLa cells (b) MCF-7 cells undergoing apoptosis induced by complexes 1 and 2 in dark and in visible light of 400-700 nm
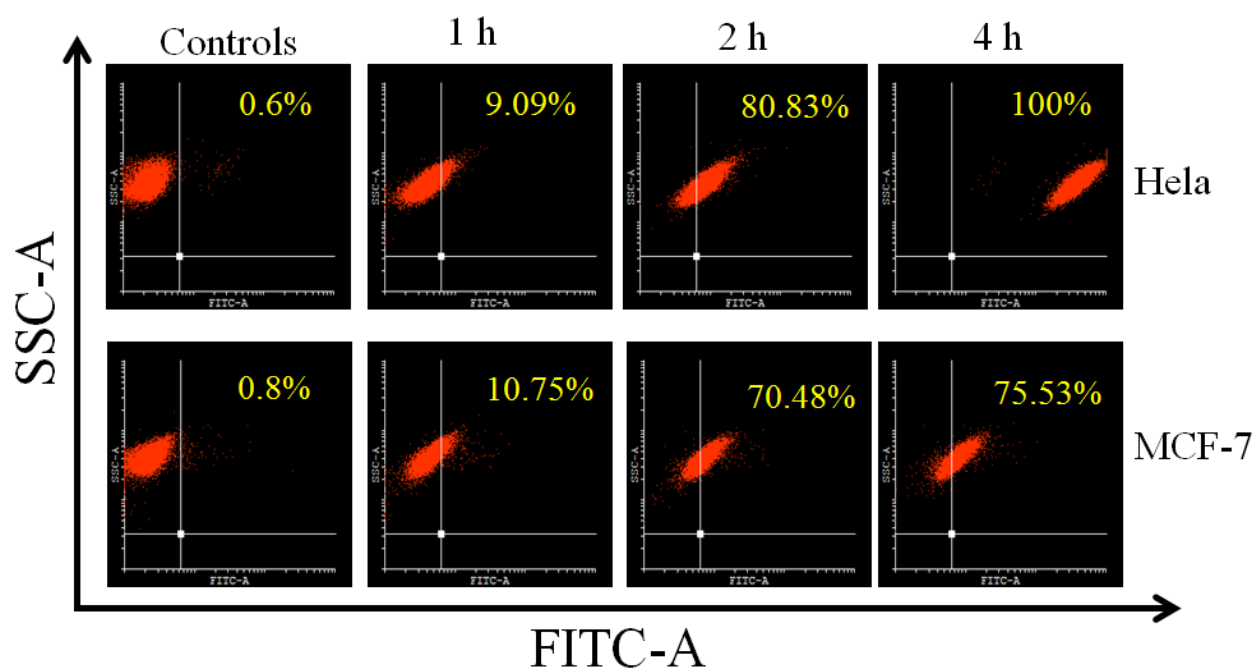
Fig. S9. Cellular incorporation data of the complex **1** (1.5 μM) in HeLa and MCF-7 cells on 1h, 2h and 4 h of incubation at 37 °C
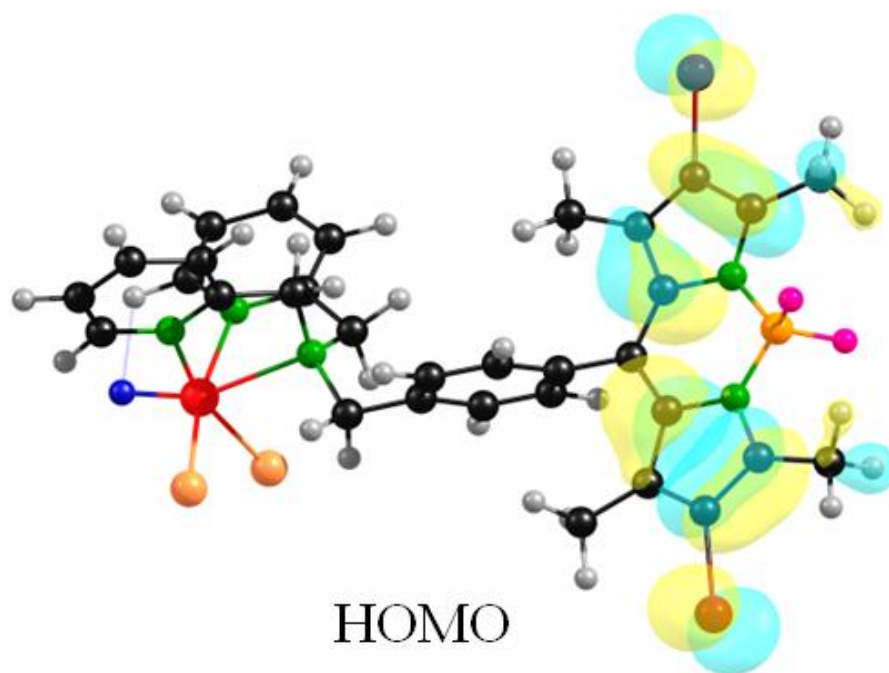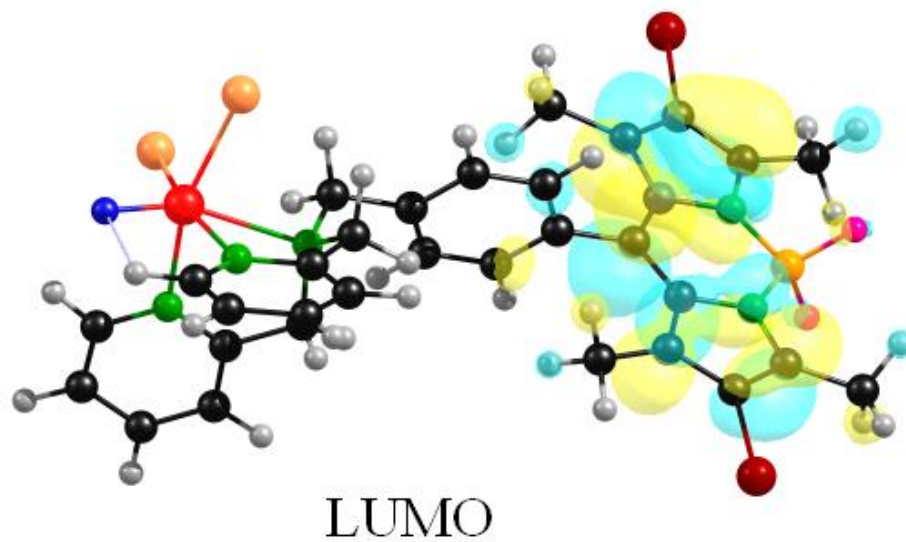
Fig. S10. HOMO and LUMO of complex 2. [colour codes: C black, N green, O blue, V red, Cl orange, I magenta, F pink, H grey]

Table S1 : Computational data for complex **2**

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Center     Atomic     Atomic            Coordinates (Angstroms)

Number     Number     Type         X            Y            Z

---------------------------------------------------------------------

    1         23          0      -6.181532    -1.274967    -0.410027
    2         17          0      -5.570149    -1.834285    -2.635562
    3         17          0      -5.530938    -3.402361     0.420224
    4          9          0       6.439231     0.936165     1.296769
    5          9          0       6.542980     0.993685    -1.035928
    6          8          0      -7.779397    -1.312853    -0.345089
    7          7          0      -6.024898    -0.691441     1.645015
    8          7          0       4.489136     1.744839     0.068052
    9          7          0       5.097579    -0.667752     0.020117
   10          6          0       7.334783    -1.809022     0.025822
   11          1          0       7.716317    -2.798230     0.291928
   12          1          0       7.742860    -1.531786    -0.955371
   13          1          0       7.700289    -1.069172     0.744306
   14          7          0      -6.243990     0.769686    -1.111657
   15          6          0      -4.910596    -0.086969     2.133054
   16          6          0      -3.911678     0.434678     1.120454
   17          1          0      -4.171317     1.480547     0.908237
   18          1          0      -2.903381     0.448734     1.553564
   19          7          0      -3.942909    -0.328057    -0.165278
   20          6          0      -2.937882    -1.465813    -0.209625
   21          1          0      -3.169043    -2.029982    -1.118342
   22          1          0      -3.177189    -2.123438     0.629528
   23          6          0      -1.471472    -1.053086    -0.170640
   24          6          0      -0.768608    -0.716210    -1.350545
   25          1          0      -1.278723    -0.758194    -2.310474
   26          6          0       0.590323    -0.360578    -1.309980
   27          1          0       1.113552    -0.113116    -2.230245
   28          6          0       1.289619    -0.343838    -0.085046
   29          6          0       0.604540    -0.696594     1.095293
   30          1          0       1.136763    -0.707224     2.043194
   31          6          0      -0.756392    -1.046662     1.048984
   32          1          0      -1.258862    -1.352411     1.965172
   33          6          0       2.742692     0.021557    -0.037730
   34          6          0       3.120865     1.384250     0.025093
   35          6          0       4.600708     3.102934     0.132488
   36          6          0       3.282125     3.647975     0.132592
   37          6          0       2.343870     2.599238     0.069680
   38          6          0       0.846960     2.752645     0.051550
   39          1          0       0.569824     3.790175     0.262649
   40          1          0       0.363518     2.109386     0.794041
   41          1          0       0.428937     2.486623    -0.927478
   42          6          0       5.919911     3.804541     0.205979
   43          1          0       6.368933     3.671858     1.199076
   44          1          0       5.799642     4.874026     0.017047
   45          1          0       6.621901     3.380697    -0.519193
   46          6          0       5.839355    -1.810854    -0.015338
   47          6          0       4.937842    -2.914989    -0.113695
   48          6          0       3.615269    -2.436225    -0.139694
   49          6          0       2.373815    -3.278649    -0.247419
   50          1          0       1.719238    -2.941328    -1.057600
   51          1          0       1.782836    -3.249066     0.675880
   52          1          0       2.639241    -4.322414    -0.438533
   53          6          0       3.720722    -0.996644    -0.049239
   54          6          0      -3.819485     0.591554    -1.335498
   55          1          0      -3.693314    -0.033789    -2.226925
   56          1          0      -2.955400     1.266912    -1.249331
   57          6          0      -5.094844     1.388091    -1.504340
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58          6          0      -7.438090    1.395505   -1.288504
59          1          0      -8.310844    0.834308   -0.974972
60          6          0      -7.528669    2.670159   -1.865497
61          1          0      -8.501700    3.131842   -1.996560
62          6          0      -6.347491    3.318689   -2.269374
63          1          0      -6.385189    4.305987   -2.721268
64          6          0      -5.115334    2.668736   -2.080077
65          1          0      -4.183778    3.138365   -2.381876
66          6          0      -4.729726    0.104718    3.514457
67          1          0      -3.822347    0.577738    3.879023
68          6          0      -5.730165   -0.319458    4.404529
69          1          0      -5.608056   -0.183724    5.475548
70          6          0      -6.888535   -0.928558    3.886705
71          1          0      -7.684598   -1.276366    4.536343
72          6          0      -6.997335   -1.107068    2.502186
73          1          0      -7.850104   -1.594781    2.045886
74          5          0       5.666775    0.757633    0.088065
75         53          0       2.856583    5.712086    0.221621
76         53          0       5.544891   -4.930844   -0.216009
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Table S2: Computational data for complex [**2 –Cl**]⁺

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 Center     Atomic     Atomic          Coordinates (Angstroms)
 Number     Number      Type        X            Y           Z
 ---------------------------------------------------------------------
     1         23          0      -6.318475   -1.590230   -0.159095
     2         17          0      -5.596417   -3.009876   -2.052062
     3          9          0       6.239666    1.123445    1.125683
     4          9          0       6.190660    1.174923   -1.203797
     5          8          0      -7.876401   -1.998591    0.079587
     6          7          0      -6.107432   -0.804866    1.774898
     7          7          0       4.169085    1.829682    0.018125
     8          7          0       4.891316   -0.553534   -0.048234
     9          6          0       7.177938   -1.642890   -0.098524
    10          1          0       7.583249   -2.191359    0.761223
    11          1          0       7.550980   -2.142494   -1.001785
    12          1          0       7.568472   -0.625810   -0.077500
    13          7          0      -6.544615    0.124604   -1.224995
    14          6          0      -4.997972   -0.069886    2.108617
    15          6          0      -4.135430    0.361967    0.945319
    16          1          0      -4.548506    1.295985    0.547121
    17          1          0      -3.113797    0.584888    1.272468
    18          7          0      -4.154632   -0.659958   -0.150599
    19          6          0      -3.099851   -1.733053    0.036802
    20          1          0      -3.275710   -2.468591   -0.753411
    21          1          0      -3.318641   -2.216587    0.996116
    22          6          0      -1.650275   -1.261361    0.021989
    23          6          0      -0.943722   -1.112120   -1.193311
    24          1          0      -1.432950   -1.339886   -2.137270
    25          6          0       0.397531   -0.693551   -1.203543
    26          1          0       0.923686   -0.591311   -2.148679
    27          6          0       1.065575   -0.413928    0.007038
    28          6          0       0.373558   -0.567504    1.225204
    29          1          0       0.879969   -0.368129    2.165649
    30          6          0      -0.966753   -0.991953    1.229231
    31          1          0      -1.476133   -1.129334    2.180653
    32          6          0       2.499647    0.022111   -0.001183
    33          6          0       2.814653    1.399998    0.020830
    34          6          0       4.205854    3.196318    0.040882
    35          6          0       2.863319    3.670282    0.056825
    36          6          0       1.977549    2.574969    0.041752
    37          6          0       0.476056    2.651260    0.047753
    38          1          0       0.145519    3.688277   -0.063105
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39          1          0       0.059495    2.264767    0.985467
40          1          0       0.037153    2.063772   -0.764881
41          6          0       5.464779    4.006656    0.045494
42          1          0       5.513752    4.628023    0.948917
43          1          0       5.480544    4.689169   -0.813599
44          1          0       6.355056    3.379284    0.007592
45          6          0       5.681269   -1.669335   -0.072212
46          6          0       4.828754   -2.809489   -0.067557
47          6          0       3.483787   -2.391384   -0.039384
48          6          0       2.279344   -3.291058   -0.020948
49          1          0       1.697868   -3.201178   -0.945855
50          1          0       1.605517   -3.048961    0.807033
51          1          0       2.584857   -4.336407    0.082414
52          6          0       3.526449   -0.949023   -0.030929
53          6          0      -4.101579   -0.005044   -1.500674
54          1          0      -3.944453   -0.799306   -2.238180
55          1          0      -3.273221    0.710638   -1.581948
56          6          0      -5.419539    0.690056   -1.789670
57          6          0      -7.764000    0.698209   -1.487184
58          1          0      -8.618426    0.220191   -1.023040
59          6          0      -7.901770    1.822546   -2.307774
60          1          0      -8.890980    2.232405   -2.483961
61          6          0      -6.754331    2.405191   -2.882762
62          1          0      -6.831619    3.281954   -3.517780
63          6          0      -5.501140    1.825099   -2.606466
64          1          0      -4.590082    2.247292   -3.019848
65          6          0      -4.735858    0.320695    3.429047
66          1          0      -3.840157    0.893313    3.649317
67          6          0      -5.643451   -0.022527    4.449177
68          1          0      -5.458312    0.272614    5.477284
69          6          0      -6.796351   -0.754494    4.102922
70          1          0      -7.530703   -1.037388    4.849883
71          6          0      -6.993042   -1.130621    2.768719
72          1          0      -7.859363   -1.699892    2.453731
73          5          0       5.376518    0.894909   -0.027005
74         53          0       2.356896    5.716638    0.098864
75         53          0       5.543002   -4.793094   -0.100858
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Table S3: Computational data for complex [**2 –2Cl**]$^{2+}$

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-------------------------------------------------------------------
Center    Atomic     Atomic          Coordinates (Angstroms)
Number    Number     Type         X           Y           Z
-------------------------------------------------------------------
   1        23          0       -6.305572   -2.022768   -0.758967
   2         9          0        5.719731    1.548501    1.390157
   3         9          0        5.853860    1.717832   -0.929415
   4         8          0       -7.840956   -2.427551   -0.915911
   5         7          0       -6.305466   -1.811596    1.259283
   6         7          0        3.666992    2.024464    0.139156
   7         7          0        4.719053   -0.231935    0.031064
   8         6          0        7.132572   -0.996430    0.106533
   9         1          0        7.542385   -1.566242    0.950066
  10         1          0        7.643126   -1.351657   -0.797794
  11         1          0        7.372268    0.056935    0.249328
  12         7          0       -6.570943   -0.075633   -1.304463
  13         6          0       -5.242908   -1.167121    1.838198
  14         6          0       -4.269201   -0.476661    0.911615
  15         1          0       -4.592907    0.563952    0.791202
  16         1          0       -3.271324   -0.439083    1.356082
  17         7          0       -4.233398   -1.134963   -0.446886
  18         6          0       -3.133423   -2.203995   -0.541787
  19         1          0       -3.280357   -2.713729   -1.500081
  20         1          0       -3.336751   -2.924291    0.257208
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21          6          0        -1.711495    -1.671874    -0.431962
22          6          0        -1.028285    -1.191535    -1.572220
23          1          0        -1.499466    -1.235910    -2.551172
24          6          0         0.266635    -0.658714    -1.464714
25          1          0         0.770531    -0.284038    -2.350991
26          6          0         0.913482    -0.606477    -0.212576
27          6          0         0.258587    -1.126232     0.922130
28          1          0         0.753917    -1.113232     1.888741
29          6          0        -1.039432    -1.654428     0.811140
30          1          0        -1.518284    -2.065901     1.696814
31          6          0         2.274600     0.009062    -0.089433
32          6          0         2.388942     1.412685     0.037103
33          6          0         3.508664     3.378519     0.251466
34          6          0         2.113066     3.659118     0.228721
35          6          0         1.393410     2.455041     0.100085
36          6          0        -0.103607     2.326444     0.047627
37          1          0        -0.574544     3.285736     0.280788
38          1          0        -0.473334     1.582334     0.760082
39          1          0        -0.445500     2.019040    -0.947818
40          6          0         4.639851     4.349884     0.385692
41          1          0         4.647636     4.791688     1.391136
42          1          0         4.517528     5.175051    -0.325987
43          1          0         5.605728     3.875942     0.210607
44          6          0         5.657500    -1.225791    -0.005021
45          6          0         4.976577    -2.466419    -0.165846
46          6          0         3.589010    -2.235658    -0.231702
47          6          0         2.525412    -3.283912    -0.406214
48          1          0         1.824726    -3.023486    -1.205408
49          1          0         1.937309    -3.414202     0.510254
50          1          0         2.978630    -4.248986    -0.650916
51          6          0         3.426435    -0.808113    -0.099287
52          6          0        -4.124675    -0.099823    -1.536342
53          1          0        -3.906312    -0.617555    -2.477496
54          1          0        -3.310822     0.608501    -1.350653
55          6          0        -5.446890     0.630643    -1.656382
56          6          0        -7.805803     0.502308    -1.398250
57          1          0        -8.652336    -0.108612    -1.110756
58          6          0        -7.960366     1.814162    -1.853184
59          1          0        -8.953161     2.243593    -1.915398
60          6          0        -6.816647     2.547835    -2.222274
61          1          0        -6.909843     3.568614    -2.578080
62          6          0        -5.548817     1.947783    -2.118661
63          1          0        -4.650173     2.492322    -2.386314
64          6          0        -5.125166    -1.099692     3.232789
65          1          0        -4.273801    -0.593048     3.673623
66          6          0        -6.115050    -1.685269     4.040166
67          1          0        -6.036039    -1.638413     5.121330
68          6          0        -7.209626    -2.331018     3.432050
69          1          0        -7.995189    -2.789341     4.020949
70          6          0        -7.276998    -2.379593     2.038574
71          1          0        -8.095741    -2.863847     1.521089
72          5          0         4.994151     1.266565     0.158162
73         53          0         1.309251     5.603064     0.377831
74         53          0         5.959297    -4.328321    -0.277825
---------------------------------------------------------------------
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Table S4. Selected bond distances (Å) and angles (°) for Complex **2** and its two proposed intermediate structures [a]

	Complex 2	Complex [2 – Cl]$^+$	Complex [2 – 2Cl]$^{++}$
V(1)-O(1)	1.60	1.62	1.59
V(1)-N(4)	2.16	2.03	2.03
V(1)-N(1)	2.14	2.09	2.02
V(1)-N(5)	2.44	2.35	2.27
V(1)-Cl(1)	2.37	2.47	-
V(1)-Cl(2)	2.37	-	-
O(1)-V(1)-N(1)	92.32	93.15	97.13
O(1)-V(1)-N(4)	90.38	100.49	95.20
O(1)-V(1)-N(5)	156.99	167.85	171.34
O(1)-V(1)-Cl(1)	106.83	104.331	-
O(1)-V(1)-Cl(2)	103.78	-	-
Cl(1)-V(1)-Cl(2)	92.64	-	-
N(1)-V(1)-Cl(1)	160.81	152.97	-
N(4)-V(1)-Cl(1)	85.76	96.62	-
N(5)-V(1)-Cl(1)	87.09	87.78	-
N(1)-V(1)-Cl(2)	83.60	-	-
N(5)-V(1)-Cl(2)	93.50	-	-
N(4)-V(1)-Cl(2)	165.56	-	-
N(4)-V(1)-N(5)	72.09	76.74	77.45
N(1)-V(1)-N(4)	93.20	100.30	99.59
N(1)-V(1)-N(5)	74.41	75.90	79.80

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[a] Significant observations include: (i) essentially no change in the V=O bond distance on dissociation of the chloride ligands; (ii) dissociation of the first chloride ligand increases the bond distance of the V-Cl bond thus making it susceptible to the visible light mediated dissociation of the same; and (iii) removal of the chloride ligands stabilizes the V-N bonds for the N,N,N tridentate ligand thus making the intermediate species stable under cellular conditions.