Electronic Supplementary Information (ESI[†]) For

Targeted photodynamic therapy in visible light by BODIPY-appended

copper(II) complexes of vitamin B₆ Schiff base

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Scheme S1. Synthetic scheme for BODIPY ligands $(L^1 \& L^2)$.



Scheme S2. Generalized synthetic scheme for the complexes.



Fig. S1. The ESI-MS of complex 1 showing the $[M + H]^+$ peak at 851 (m/z) in methanol (Inset: Isotopic distribution pattern observed).



Fig. S2. The ESI-MS of complex **2** showing the $[M + H]^+$ peak at 1103 (m/z) in methanol (above) ; Isotopic distribution pattern observed (below).



Fig. S3. The ESI-MS of complex **3** showing the $[M + H]^+$ peak at ~515 (m/z) in methanol; (Inset: Isotopic distribution pattern observed).



Fig. S4. IR spectra of complexes 1-3 in the solid phase [1, (a); 2, (b); 3, (c)].



Fig. S5. UV-vis absorption spectra of the complexes **1-3** showing Cu(II)-centred low energy d-d bands in 20% DMSO/DPBS.



Fig. S6. (a) UV-visible absorption spectra of the ligands in 20% DMSO/DPBS. (b) Emission spectra of ligands in 20% DMSO/DPBS.



Fig. S7. Cyclic voltammograms of complex **1** showing cathodic (a); anodic (b); and small scan (c) in 0.1 M TBAP-DMF at a scan rate of 100 mV s⁻¹.



Fig. S8. Cyclic voltammograms of complex **2** showing cathodic (a); anodic (b); and small scan (c) in 0.1 M TBAP-DMF at a scan rate of 100 mV s⁻¹.



Fig. S9. Cyclic voltammograms of complex 3 showing cathodic (a); anodic (b); and small scan (c) in 0.1 M TBAP-DMF at a scan rate of 100 mV s⁻¹.



Fig. S10. Cyclic voltammograms of ligands showing cathodic scans for ligand L^1 (a); ligand L^2 (b); and ligand L^3 (c) at a scan rate of 100 mV s⁻¹.



Fig. S11. The unit cell packing diagram of complex **3** with four complex molecules in the unit cell with colour codes: C, grey; N, green; O, blue and Cu, red.



Fig. S12. The time-dependent UV-visible spectra of complexes 1-3 in 10% DMSO/DPBS in dark [complexes: 1, (a); 2, (b); 3, (c)].



Fig. S13. Histogram showing time-dependent incorporation of the complex 1 (12 μ M) (black, Unstained; blue, 1h; red, 2h; green, 4h) in HeLa cells.



Fig. S14. Histogram showing the change in uptake of complex 1 (2 μ M) in HeLa cells on pre-treating the cells with VB₆ for 1 h (black, Unstained; red, Complex 1 only; blue, Complex 1 + VB₆).

Fig. S15. Histogram showing the change in uptake of complex 1 (2 μ M) in HPL1D cells on pre-treating the cells with VB₆ for 1 h (black, Unstained; red, Complex 1 only; blue, Complex 1 + VB₆).

Fig. S16. Photocytotoxicity of complexes 1-3 in HeLa cells upon irradiation with visible light (400-700 nm, 10 $J \text{ cm}^{-2}$, red symbol) and in dark (black symbol) post 4 h of incubation with the complexes: 1 (a); 2 (b); 3 (c).

Fig. S17. Photocytotoxicity of complexes 1-3 in MCF-7 cells upon irradiation with visible light (400-700 nm, $10 J \text{ cm}^{-2}$, red symbol) and in dark (black symbol) post 4 h of incubation with the complexes: 1 (a); 2 (b); 3 (c).

Fig. S18. Photocytotoxicity of complexes 1-3 in HepG2 cells upon irradiation with visible light (400-700 nm, $10 J \text{ cm}^{-2}$, red symbol) and in dark (black symbol) post 4 h of incubation with the complexes: 1 (a); 2 (b); 3 (c).

Fig. S19. Photocytotoxicity of complexes 1-3 in HPL1D cells upon irradiation with visible light (400-700 nm, $10 J \text{ cm}^{-2}$, red symbol) and in dark (black symbol) post 4 h of incubation with the complexes: 1 (a); 2 (b); 3 (c).

Fig. S20. Absorption spectral traces of DPBF (50 μ M) in presence of L² (5 μ M) in DMF solutions, after each photoexposure of 10 s (400-700 nm, J = 10 J cm⁻²).

Fig. S21. Colocalization pixel map of complex **1** and MitoTracker Red CMXRos (mitochondria) in HeLa cells: It shows a positive colocalization between both the pixels with a Pearson's R value (above threshold) 0.7. The software merges the green (complex **1**) and red (MitoTracker red) channel and highlights colocalized pixels in white. Scale bar represents 20 μ m.

Fig. S22. Confocal images of complex 1 treated HeLa cells [panels: (a) transmitted light image; (b) fluorescence of complex $1(5 \mu M)$. The scale bar is 10 μm .

Fig. S23. Confocal images of MTR treated HeLa cells [panels: (a) transmitted light image; (b) fluorescence of MTR (100 nM). The scale bar is 10 μm.

Fig. S24. Absorption spectral traces of complex 1 in 5 mM Tris-HCl buffer (pH 7.2) on increasing concentration of calf thymus DNA. The inset shows the plot of $\Delta \epsilon_{af} / \Delta \epsilon_{bf}$ vs. [DNA].

Fig. S25. Absorption spectral traces of complex 2 in 5 mM Tris-HCl buffer (pH 7.2) on increasing concentration of calf thymus DNA. The inset shows the plot of $\Delta \varepsilon_{af} / \Delta \varepsilon_{bf}$ vs. [DNA].

Fig. S26. Absorption spectral traces of complex 3 in 5 mM Tris-HCl buffer (pH 7.2) on increasing concentration of calf thymus DNA. The inset shows the plot of $\Delta \epsilon_{af} / \Delta \epsilon_{bf}$ vs. [DNA].

Fig. S27. Gel diagram showing the mechanistic aspects of photo nuclease activity of complex 2 in the presence of various singlet oxygen quenchers and hydroxyl radical scavengers in monochromatic light of 532 nm, where $[\text{complex}] = 20 \,\mu\text{M}$, incubation time: 1 h, exposure time: 1 h.

Fig. S28. Gel diagram showing (a) DNA cleavage activity of the ligands L^1 and L^2 and complexes 1-3 in dark and light of 532 nm, where [ligand] = [complex] = 20 μ M, incubation time: 1 h, exposure time: 1 h. (b) Chemical nuclease activity of complexes 1-3 in dark in presence of GSH.

$C_{26} H_{21} Cu N_5 O_3$
515.02
Monoclinic
P 2 ₁ /c
14.291(2)
13.296(2)
12.436(2)
90
107.673(4)
90
2251.4(7)
4
59.6
273(2)
19,18,17
1.519
0.71073
1.01
0 / 320
1060
1.025
0.1021 [0.1819]
0.2352 [0.2245]

Table S1.Selected crystallographic parameters

 ${}^{a}R = \Sigma ||Fo| - |Fc|| / \Sigma |Fo|. {}^{b}wR = \{\Sigma [w (Fo^{2} - Fc^{2})^{2}] / \Sigma [w (Fo)^{2}]\}^{1/2}, w = [\sigma (Fo)^{2} + (AP)^{2} + BP]^{-1}, where P = (Fo^{2} + 2Fc^{2})/3$

bond	bond length
Cu(1)-O(1)	1.983(5)
Cu(1)-O(2)	1.906(4)
Cu(1)-N(1)	2.232(5)
Cu(1)-N(3)	2.057(6)
Cu(1)-N(4)	1.946(5)
bond	bond angle
N(1)-Cu(1)- N(3)	78.0 (2)
N(3)-Cu(1)-O(1)	93.2 (2)
N(1)-Cu(1)- N(4)	101.5 (2)
N(4)-Cu(1)- O(2)	93.2 (2)
N(3)-Cu(1)- O(2)	89.1 (2)
N(1)-Cu(1)-O(1)	94.2 (2)
N(1)-Cu(1)- O(2)	107.9 (2)
O(1)-Cu(1)- O(2)	157.7 (2)
N(3)-Cu(1)- N(4)	177.7 (2)
N(4)-Cu(1)- O(1)	84.5 (2)

Table S2.Selected bond distances (Å) and angels (°) for complex ${\bf 3}$

Table S3. Optimized coordinates of complexes 1-3 as obtained from DFT calculations usingB3LYP/LANL2DZ level of theory

	-	complex 1	
Atomic	Coordinates (Angstroms)		
Number	Х	Y	Z
6	-2.099780134	-1.600210770	1.153959719
6	-2.780034535	-2.265260348	2.192700839
1	-3.671713715	-1.830451452	2.633469455
6	-2.268443751	-3.497080646	2.621856258
1	-2.770894803	-4.039282164	3.418361164
6	-1.101256549	-4.059504778	2.032982053
1	-0.736423798	-5.017649737	2.394566999
6	-0.409898452	-3.407030929	1.000414511
1	0.485073970	-3.842845155	0.565089725
6	-0.928828682	-2.171655856	0.575524550
6	-1.425389986	-0.210333797	-0.395204872
6	-1.416389803	0.977496982	-1.263619331
6	-0.252929742	1.583929907	-1.779027986
1	0.725643516	1.169950005	-1.564274645
6	-0.373551573	2.765954398	-2.530221116
1	0.513780713	3.245131822	-2.934478058
6	-1.644134350	3.333920827	-2.728661865
1	-1.773567560	4.253080086	-3.290127112
6	-2.760512440	2.688171211	-2.169766196
1	-3.763924840	3.089537925	-2.261315432
6	-4.841170120	-1.923172821	-1.883666575
6	-4.772800371	-3.134791010	-2.623129480
1	-3.929612703	-3.279175022	-3.293025025
6	-5.774630854	-4.102724483	-2.490220820
1	-5.710450809	-5.024716772	-3.064703732

Complex 1

6	-6.873819897	-3.895728436	-1.618502062
1	-7.646380156	-4.654149857	-1.523287311
6	-6.962157413	-2.707998705	-0.881684948
1	-7.810097596	-2.556382973	-0.218514119
6	-5.955617464	-1.722042142	-1.002274082
6	-6.866818882	-0.070709014	0.516418926
6	-6.917563540	1.216166520	1.182060364
6	-7.978202020	1.512620310	2.134400847
6	-8.011212468	2.798285917	2.713730885
1	-8.796391382	3.025022466	3.426968528
6	-6.128139302	3.539007793	1.566609169
6	-5.968024183	2.256529198	0.901397219
6	-5.146188669	4.639535553	1.268644060
1	-5.386321859	5.516236038	1.875038996
1	-5.175326015	4.907070732	0.203318791
1	-4.119806611	4.308006218	1.472996856
6	-9.094866083	0.708633891	2.670334604
7	-2.381804736	-0.381564399	0.525414686
7	-0.510956433	-1.269643152	-0.417726684
7	-2.644041591	1.536233823	-1.476114414
7	-5.927831425	-0.472807467	-0.319210828
7	-7.117130516	3.789841984	2.442593237
8	-3.901760824	-0.963367129	-1.995583806
8	-4.940345572	2.147149573	0.063586142
8	-9.106372672	-0.584361096	2.170439278
1	-9.862638400	-1.065907355	2.562735428
29	-4.289940864	0.533296598	-0.780995318
1	-7.693360989	-0.736344538	0.741402038
6	7.953374823	2.958541367	-0.085676875
6	6.716890214	3.491120104	-0.543091309
6	5.773492277	2.453305087	-0.602569487
6	6.457909545	1.257487548	-0.169284027

6	6.031169793	-0.080361705	-0.019061146
6	6.921782776	-1.073759943	0.440638159
6	6.755019657	-2.486997151	0.693577041
6	7.998196242	-2.954835354	1.146551803
6	8.913505874	-1.866598164	1.175340914
6	9.246799751	3.678713555	0.139524964
1	9.543761746	3.621079496	1.194009996
1	9.153661168	4.729779303	-0.148982885
1	10.055310249	3.215531350	-0.438529811
6	4.341157141	2.627611426	-1.037621333
1	4.092369326	1.989284173	-1.894034533
1	4.165151328	3.669605933	-1.326988783
1	3.637496929	2.377415984	-0.234151988
6	10.353519938	-1.876839611	1.585874454
1	10.520600934	-1.196833506	2.430069120
1	10.992733828	-1.522289653	0.768156388
1	10.661919782	-2.886729702	1.871400728
6	5.527177095	-3.345434194	0.532972392
1	4.703817698	-3.005654039	1.172839059
1	5.758493859	-4.381452041	0.803417596
1	5.153226954	-3.340180718	-0.497736970
6	4.618549495	-0.450981904	-0.360900472
6	4.287364379	-0.866206191	-1.668805022
1	5.063149953	-0.916171313	-2.428596298
6	2.965290261	-1.211272012	-1.993207551
1	2.729447693	-1.528077339	-3.008148226
6	1.943375681	-1.150803695	-1.020220292
6	2.274777230	-0.736787459	0.284810447
1	1.504820719	-0.683730656	1.049084011
6	3.599916592	-0.390472085	0.609964565
1	3.840922321	-0.073900807	1.621574196
7	7.794167879	1.621128766	0.136757428

7	8.265314916	-0.742223777	0.752912474
5	8.883937460	0.655944300	0.622643900
9	9.985243477	0.630611436	-0.317576534
9	9.409784385	1.093311349	1.897782320
6	0.523651999	-1.560087022	-1.415672212
1	0.495828210	-2.640867576	-1.607525556
1	0.242285848	-1.078018571	-2.358365190
1	8.235021370	-3.970580801	1.431421776
1	6.546188058	4.527792887	-0.798454876

Complex 2

Atomic	Coordinates (Angstroms)		
Number	Х	Y	Z
6	-3.454001786	-1.945708024	0.389483813
6	-4.079205883	-2.993394965	1.093469293
1	-4.971529352	-2.805663452	1.682396368
6	-3.513089384	-4.271468027	0.995855215
1	-3.972241016	-5.103743769	1.522502764
6	-2.346572041	-4.507537930	0.215552667
1	-1.939062781	-5.514168648	0.166091781
6	-1.709952083	-3.473369689	-0.488206391
1	-0.814961624	-3.663516241	-1.073846056
6	-2.283620962	-2.194507730	-0.385228357
6	-2.877137576	-0.032952854	-0.502774001
6	-2.930120845	1.400341905	-0.832014736
6	-1.800334562	2.206560700	-1.079316251
1	-0.803477064	1.781063911	-1.055769144
6	-1.977630118	3.583245736	-1.300720911

1	-1.116881295	4.218041710	-1.491681623
6	-3.270534436	4.132454418	-1.245143563
1	-3.443740119	5.192623338	-1.396159658
6	-4.350634975	3.275210135	-0.972945364
1	-5.368049369	3.640399355	-0.885579338
6	-6.324252655	-1.152996796	-2.458478143
6	-6.264088006	-1.976500827	-3.614982675
1	-5.446679710	-1.819828711	-4.313459792
6	-7.241641530	-2.951969684	-3.841009699
1	-7.184151979	-3.573595903	-4.732347014
6	-8.307958029	-3.138099997	-2.924799010
1	-9.062130438	-3.898165805	-3.110843321
6	-8.387923856	-2.335984268	-1.779611960
1	-9.211186863	-2.483162029	-1.084966700
6	-7.405494122	-1.348619020	-1.535367518
6	-8.286133331	-0.449637473	0.533372683
6	-8.335566582	0.475451110	1.648417415
6	-9.364804478	0.345304051	2.669878925
6	-9.399421931	1.303130642	3.704759321
1	-10.161845959	1.210862810	4.470808747
6	-7.572700691	2.488339727	2.886643944
6	-7.416580861	1.572587258	1.768699065
6	-6.619818627	3.645517235	3.016971902
1	-6.851833270	4.207978616	3.924607438
1	-6.691154049	4.307640049	2.143039332
1	-5.581624777	3.289967671	3.047704410
6	-10.445753257	-0.638214787	2.881640731
7	-3.796355738	-0.591235357	0.293494666
7	-1.929155540	-0.959354637	-0.953819660
7	-4.179605762	1.948699135	-0.790822584
7	-7.373482444	-0.464147925	-0.419825515
7	-8.532706963	2.348247903	3.817867814

8	-5.407858844	-0.195388567	-2.213908617
8	-6.420686689	1.831042813	0.925120584
8	-10.449957147	-1.638116224	1.921553401
1	-11.182011957	-2.257641857	2.116522271
29	-5.775562736	0.696060422	-0.502252931
1	-9.089922456	-1.177587943	0.505232662
6	6.763400449	2.824456578	0.255275524
6	5.577760725	3.511032674	-0.147414007
6	4.558833308	2.573036757	-0.398115267
6	5.147389975	1.279945397	-0.141032265
6	4.617187313	-0.029246447	-0.209585351
6	5.412506184	-1.147568866	0.125400249
6	5.131648614	-2.565163177	0.130541618
6	6.322567331	-3.186040599	0.550103299
6	7.314853150	-2.188140320	0.796632808
6	8.095939513	3.381397408	0.645637573
1	8.201245997	3.387662020	1.738812198
1	8.208735337	4.406199137	0.282016351
1	8.905599331	2.761317171	0.249702968
6	3.155944643	2.890212715	-0.839645382
1	2.954351998	2.508139015	-1.847654433
1	3.001762485	3.973247712	-0.853506572
1	2.410692893	2.446965787	-0.170096207
6	8.735463289	-2.351481081	1.236198837
1	8.999215390	-1.592768707	1.979233361
1	9.416056353	-2.216088229	0.384972294
1	8.899114370	-3.347466833	1.655436121
6	3.847940688	-3.264115415	-0.225869276
1	3.053245754	-3.039363598	0.495885690
1	3.995756330	-4.348050283	-0.231804855
1	3.480741626	-2.964477551	-1.213078194
6	3.198527457	-0.230530853	-0.651374552

6	2.887234114	-0.327777439	-2.024761263
1	3.682529548	-0.260151388	-2.762719940
6	1.559807759	-0.515348748	-2.441572259
1	1.340210356	-0.592505510	-3.505359608
6	0.512125520	-0.602952950	-1.498458272
6	0.824811819	-0.508317063	-0.128447827
1	0.035350716	-0.586382606	0.613619719
6	2.156091991	-0.324845968	0.290545951
1	2.381741886	-0.254790285	1.351580317
7	6.490743089	1.488090150	0.254904073
7	6.755851577	-0.971519517	0.539229807
5	7.481292465	0.379472573	0.645740630
9	8.626230680	0.394364321	-0.235227380
9	7.954320939	0.594131142	1.993125439
53	5.423029721	5.607305749	-0.316246153
53	6.643486133	-5.256164349	0.787055837
6	-0.919075591	-0.795904432	-2.002688719
1	-0.962658095	-1.684014132	-2.646627141
1	-1.211563758	0.050221201	-2.634459366

Complex 3

Atomic	Coordinates (Angstroms)		
Number	Х	Y	Z
6	-1.933136059	0.960174216	1.952068640
6	-1.113047517	1.857623767	2.663997135
1	-0.051954863	1.925678359	2.446162406
6	-1.718549705	2.649835542	3.647983074
1	-1.115772505	3.354125819	4.214790794
6	-3.112228051	2.556615445	3.922812913

1	-3.541474526	3.191098930	4.694092870
6	-3.944340553	1.668630272	3.223163129
1	-5.007127482	1.606372711	3.439794129
6	-3.331158056	0.876025858	2.238348107
6	-2.753348481	-0.551119007	0.595703804
6	-2.828397547	-1.569763912	-0.455910598
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6	-3.919162601	-3.330090568	-1.718998548
1	-4.787148907	-3.950118052	-1.924392596
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6	-0.785534823	3.189085104	-2.785349279
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1	-0.356884902	5.196186108	-3.442038385
6	1.320604127	4.361521993	-2.341770213
1	1.936650897	5.251217536	-2.442638932
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6	2.554342301	0.694673846	-0.282696756
6	2.999942872	-0.529840716	0.352923711
6	4.307390082	-0.596727249	0.990323106
6	4.717715888	-1.829826039	1.539694917
1	5.689908201	-1.885813330	2.017603548
6	2.759841142	-2.931609018	0.937884979
6	2.205711603	-1.727708800	0.339753001
6	1.942505550	-4.194785026	0.914334655

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1	1.700165960	-4.480837466	-0.118059350
1	0.980316856	-4.041895918	1.421093167
6	5.363426370	0.409993614	1.213782159
7	-1.613114668	0.058527995	0.929040364
7	-3.825771966	-0.096282639	1.359600860
1	-4.792138699	-0.373786934	1.265172752
7	-1.689657162	-1.730521239	-1.188265444
7	1.378003338	0.887831448	-0.848960971
7	3.973336868	-2.970525999	1.516522346
8	-1.050283635	0.925329270	-1.968723187
8	0.990752475	-1.834489683	-0.187857337
8	5.010321326	1.665108655	0.740774958
1	5.744843097	2.285992163	0.921297098
29	-0.126502128	-0.403456901	-0.860611925
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