Supplementary material

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{22}H_{28}ClMnN_2O_{10}$
Formula weight	590.89
Temperature [K]	293(2)
Wavelength [Å]	1.5418
Crystal system	Monoclinic
Space group	P21/c
a [Å]	13.7192(13)
b [Å]	15.7383(10)
c [Å]	13.6309(10)
α [°]	90
β [°]	119.689(4)
γ [°]	90
Volume [$Å^3$]	2556.8(3)
Z	4
$D_{calcd.}$ [g cm^{-3}]	1.535
μ [mm^{-1}]	5.715
F(000)	1232
$\theta_{min/max}$[°]	0.982/65.089
Total data	3572
Unique data	3020
R_{int}	0.0984
Restraints/parameters	7/361
GOF	1.066
Final *R* indices [I>2σ(I)]	R_1= 0.0794, wR_2= 0.2112
R indices (all data)	R_1 = 0.0899 wR_2 = 0.2202

Table S2. Selected hydrogen bond geometry (Å, °) for **1**.

D–H...A	d(D–H)	d(H...A)	d(D…A)	<(D–H···A)
O27–H27A…O32[c]	0.89	1.96	2.8278	164
O27–H27B…O29[b]	0.89	1.97	2.7785	151
O28–H28A…O19[a]	0.79	2.32	2.9813	142
O28–H28A…O20[a]	0.79	2.41	3.0739	143'
O28–H28B…O21[a]	0.77	2.18	2.8821	153
O28–H28B…O22[a]	0.77	2.39	3.0018	139
O29–H29A…O19[d]	0.85	2.29	2.9752	137
O29–H29A…O20[d]	0.85	2.46	3.2467	154
O29–H29B…O34	0.85	2.02	2.8927	175

Symmetry operations: [a] -x,1-y,-z; [b] -1+x,1/2-y,-1/2+z; [c] 1-x,1/2+y,3/2-z; [d] 1-x,1-y,1-z

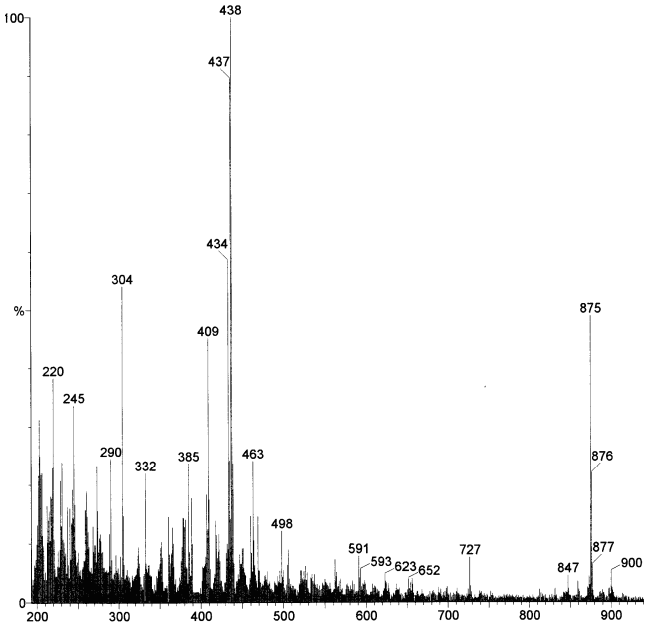

Figure S1. FAB mass spectrum of **1**, showing $[MnL]^+$ and $[Mn_2L_2]^+$ peaks.

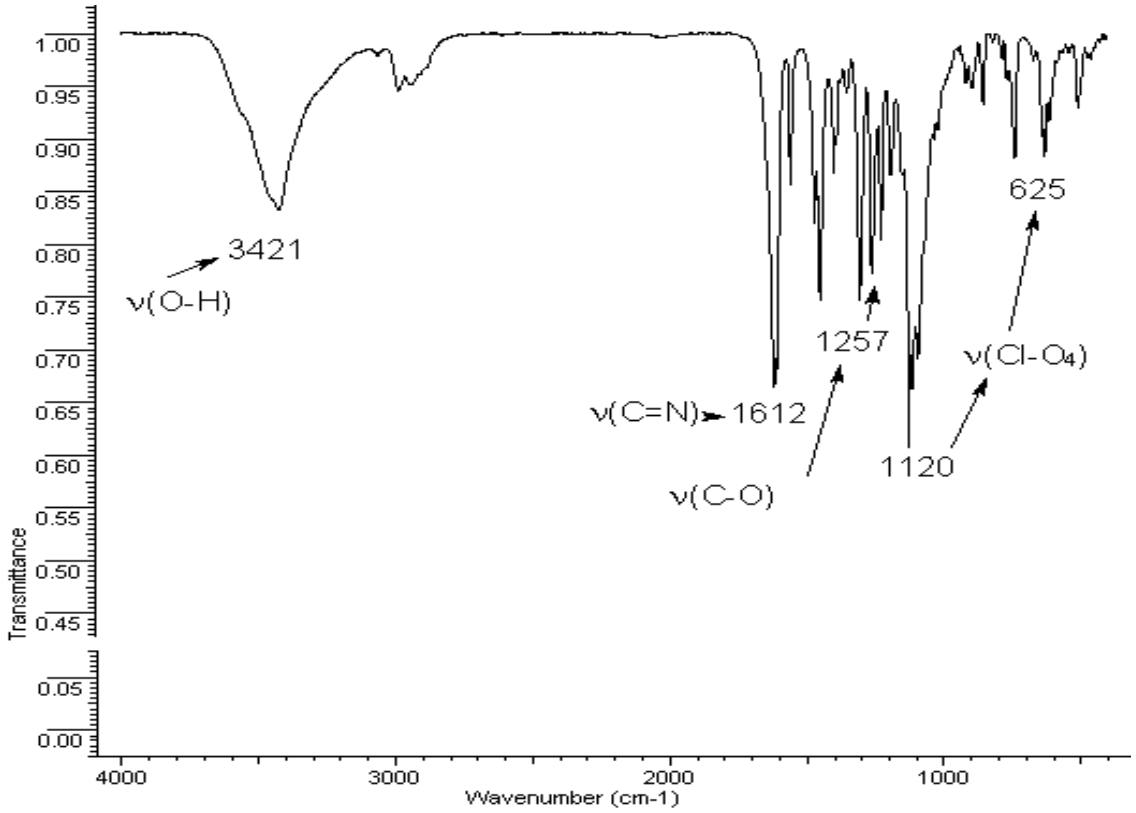

Figure S2. IR spectrum of **1**.

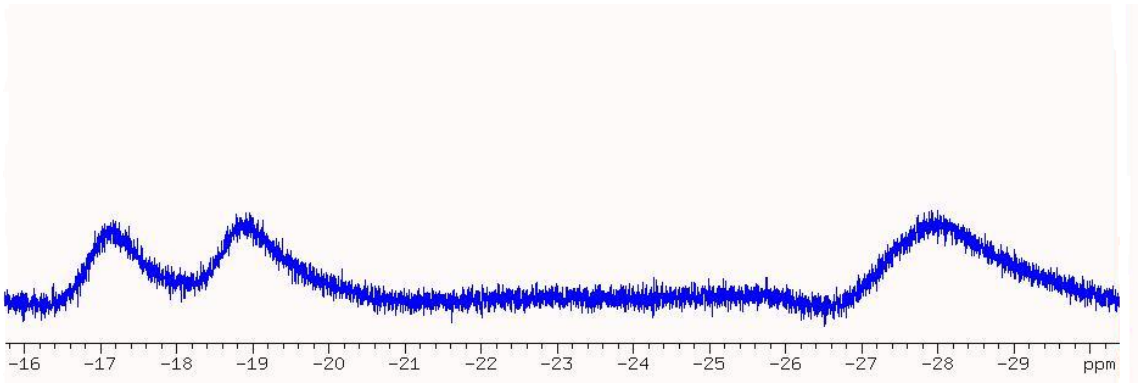

Figure S3. Paramagnetic ^{1}H NMR spectrum of **4**.

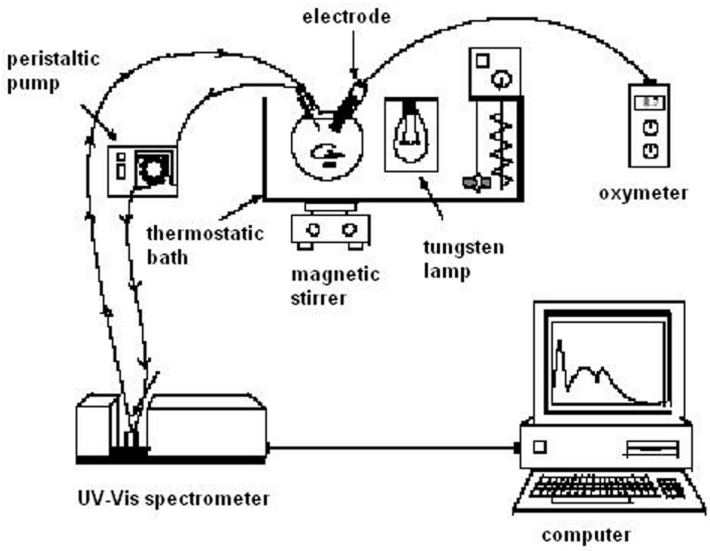

Figure S4. Setting up of the photolytic experiments.

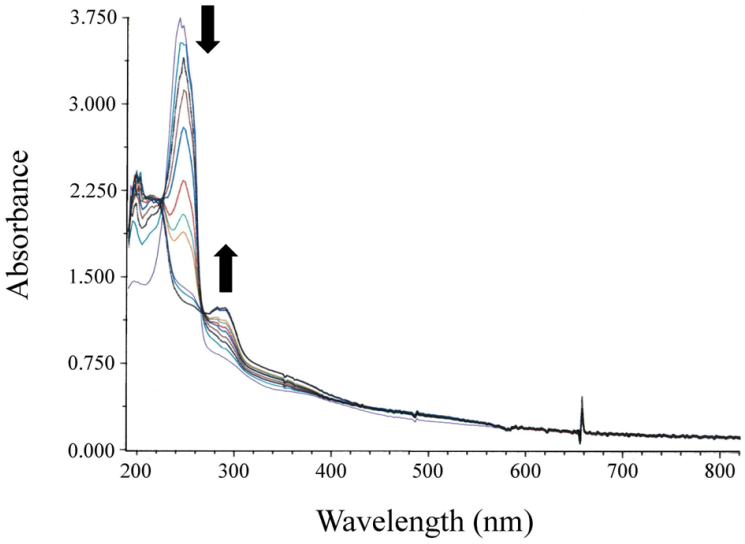

Figure S5. Evolution of the UV spectra during water photolysis experiments, showing the decrease of the 246 nm band (disappearance of BQ) and increase of the 290 nm band (formation of H_2BQ).

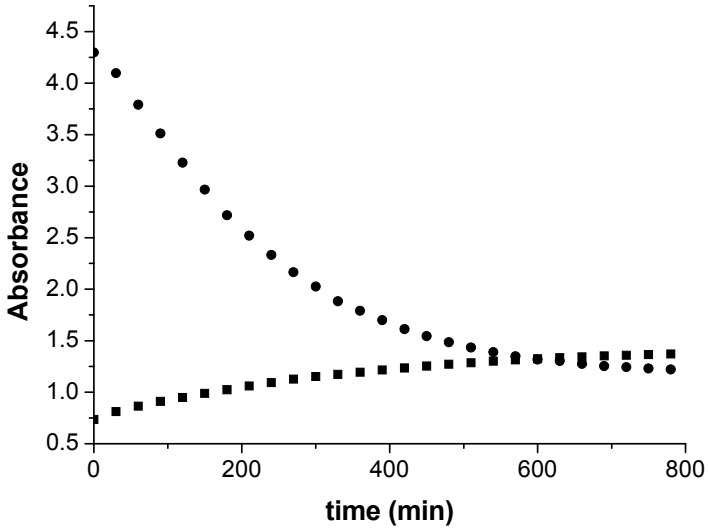

Figure S6. Variation of the absorbance at 246 nm (●) and at 290 nm (■) versus time.

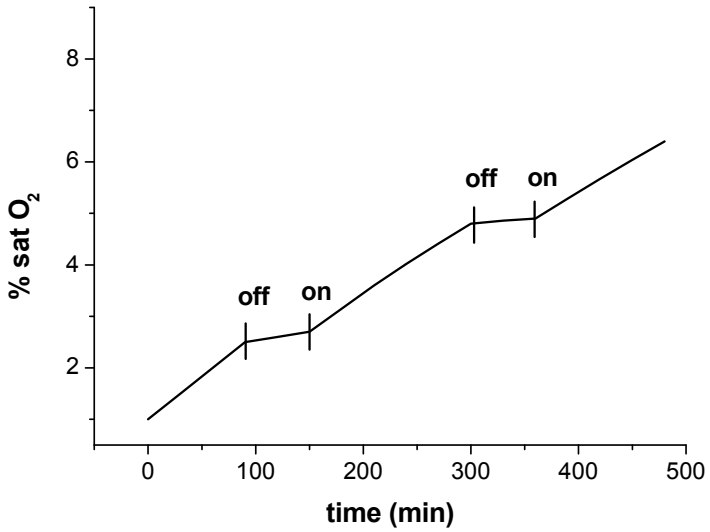

Figure S7. Plot of disolved O_2 versus time for irradiation of a solution of **4** and benzoquinone in deoxygenated distilled water. The momentums of *ligth off* and *light on* are marked in the figure.

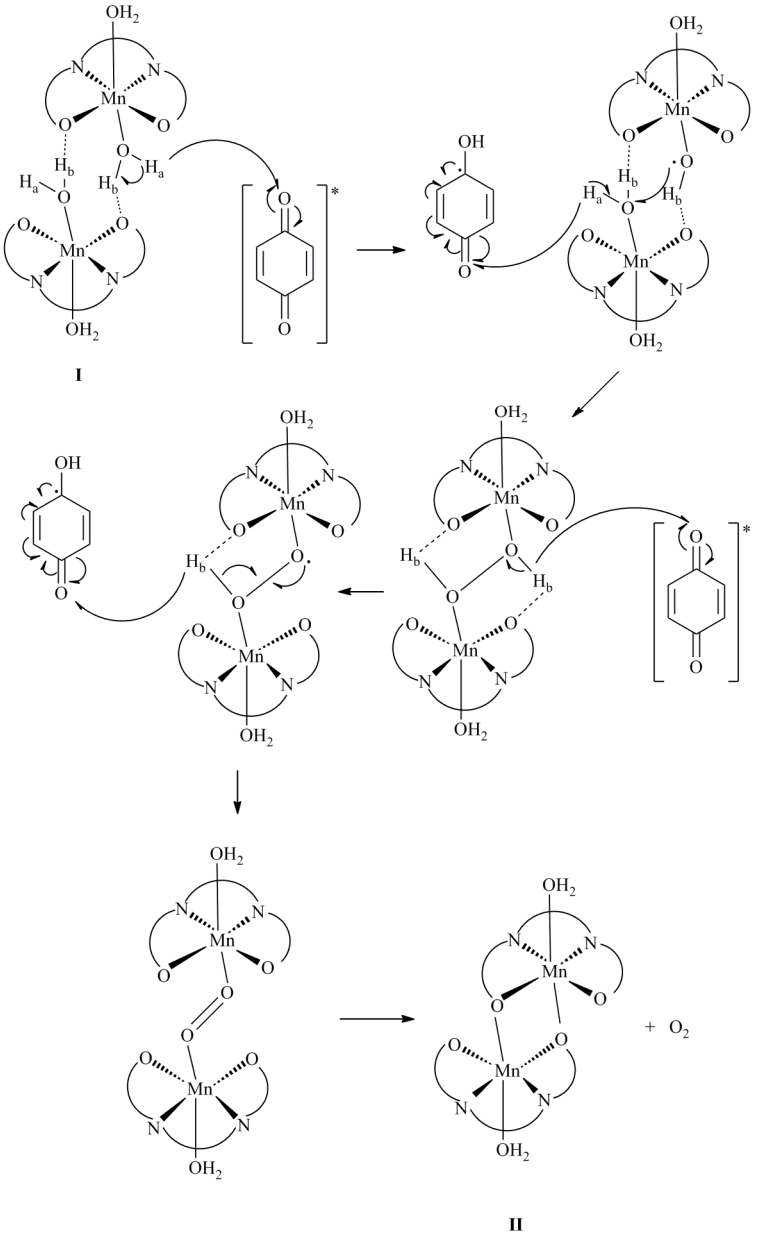

Figure S8. Proposed mechanism for the evolution of dioxygen and conversion of **I** to **II**.