Electronic Supplementary Material (ESI) for New Journal of Chemistry.

ESI

Spectrophotometric and photocatalytic studies of H-bonded charge transfer complex of oxalic acid with imidazole: Single crystal XRD, experimental and DFT/TD-DFT studies

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Figure S1. FTIR spectra of (A) Oxalic acid; (B) Imidazole; (C) chargetransfer complex of imidazole with oxalic acid.

Figure S2: Electronic absorption spectra of IZ, donor (1×10^{-4} M);OX, acceptor (1×10^{-4} M); Acceptor-donor complex (1×10^{-4} M+ 1×10^{-4} M) in (A) Ethanol, (B) Acetonitrile, (C) DMF, (D) DMSO at room temperature.

Figure S3: Comparison between **(a)** Experimental and **(b)**simulated UV-Vis spectra of $[(IZ)^{+}(OX)^{-}]$.

Figure S4: (A) and (B) are the ^{1}HNMR Spectrum of Charge Transfer Complex [(IZ)+(OX)].

Figure S5: Simulated NMR spectra of $[(IZ)^{+}(OX)^{-}]$ in (A) Vacuum and (B) DMSO.

Figure S6: **(a)**Packing structure of complex $[(IZ)^{+}(OX)^{-}]$ showing mean interplanar distance between N2C3 and N1C2 are 5.286 and 6.901**(b)** CPK representation of packing structure of crystal.

Figure S7:PXRD pattern of the CT complex.

Figure S8: **(a)**Hirshfeld Surface (**b**) 2D fingerprint plots of the CT complex.

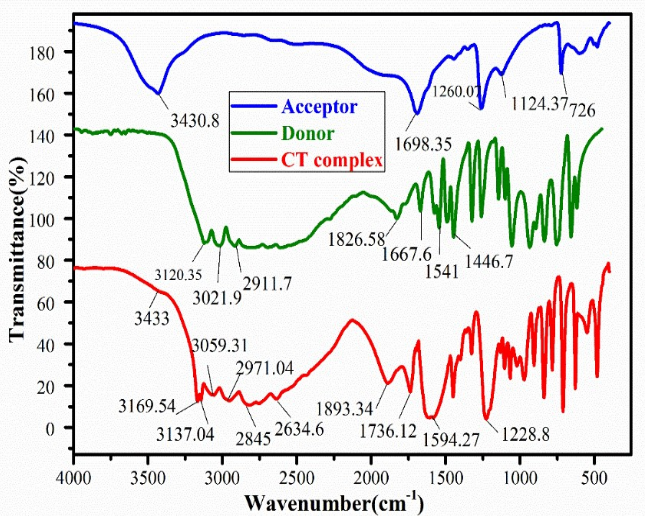
Figure S9: Energy minimized charge transfer complex with atom numbering.

Figure S10: Molecular electrostatic potential(MEP) map.

FigureS11: Degradation of the MR in the presence of acceptor **a)**Oxalic acid and donor **b)** Imidazole.

Figure S12: Cyclic Voltammogram of the prepared sample.

Figure S13: Rate of mineralization as function of time during degradation of methyl red under UV light.



FigureS1. FTIR spectra of (A) Oxalic acid; (B) Imidazole; (C) charge transfer complex of imidazole with oxalic acid.

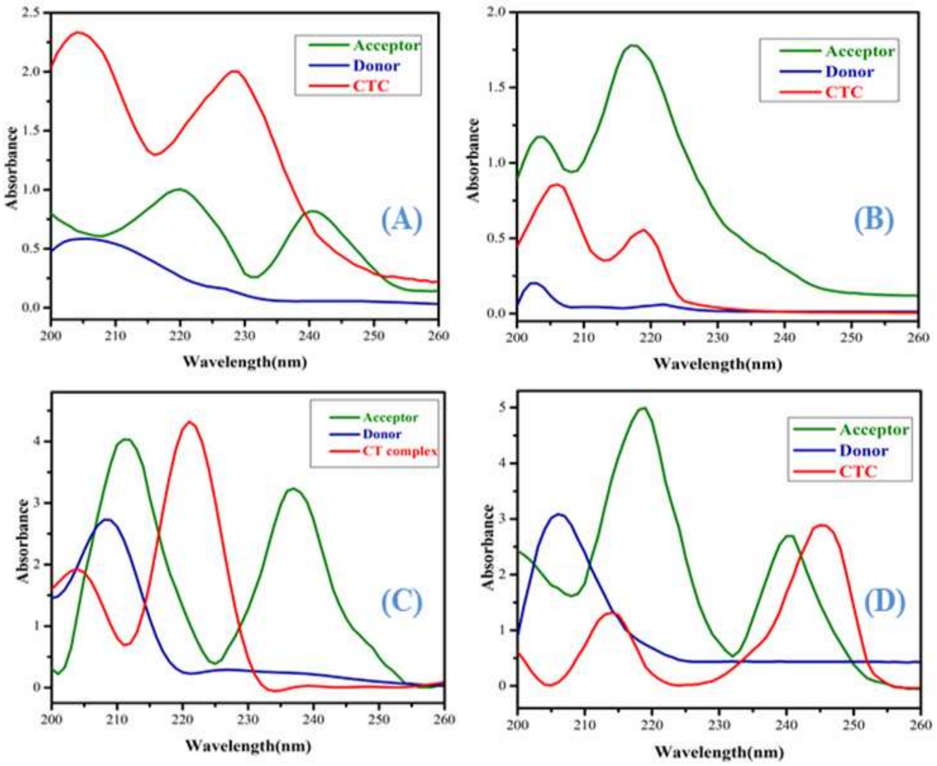


Figure S2: Electronic absorption spectra of IZ, donor (1×10^{-4} M);OX, acceptor (1×10^{-4} M); Acceptor-donor complex (1×10^{-4} M+ 1×10^{-4} M) in (A) Ethanol, (B) Acetonitrile, (C) DMF, (D) DMSO at room temperature.

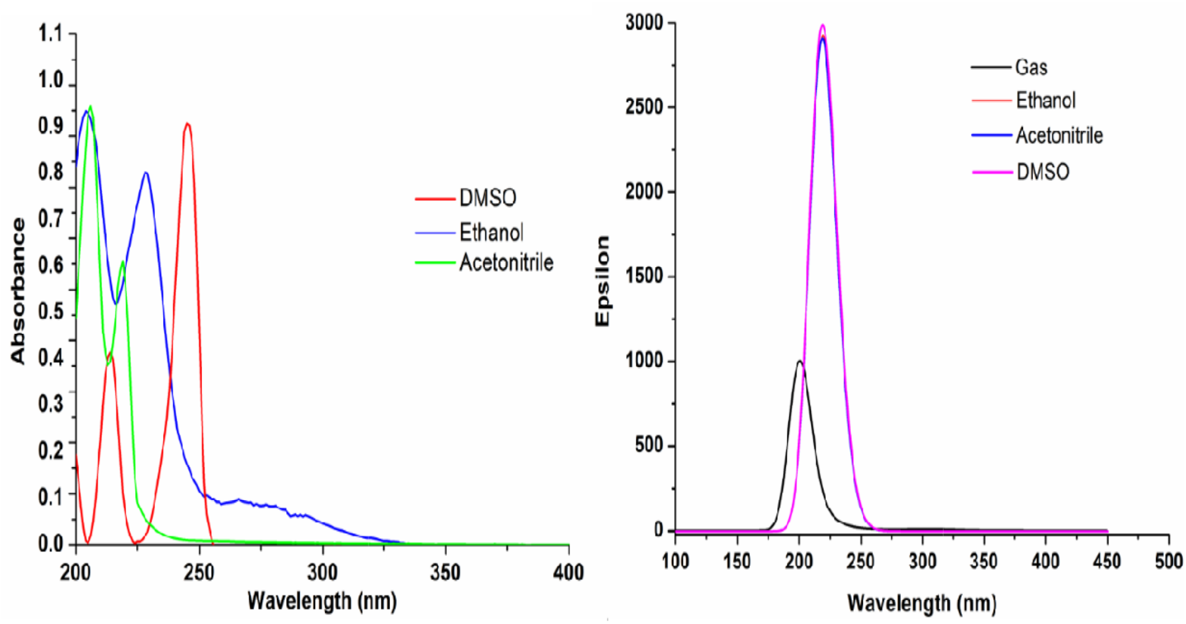


Figure S3: Comparison between **(a)** Experimental and **(b)**simulated UV-Vis spectra of $[(IZ)^{+}(OX)^{-}]$.

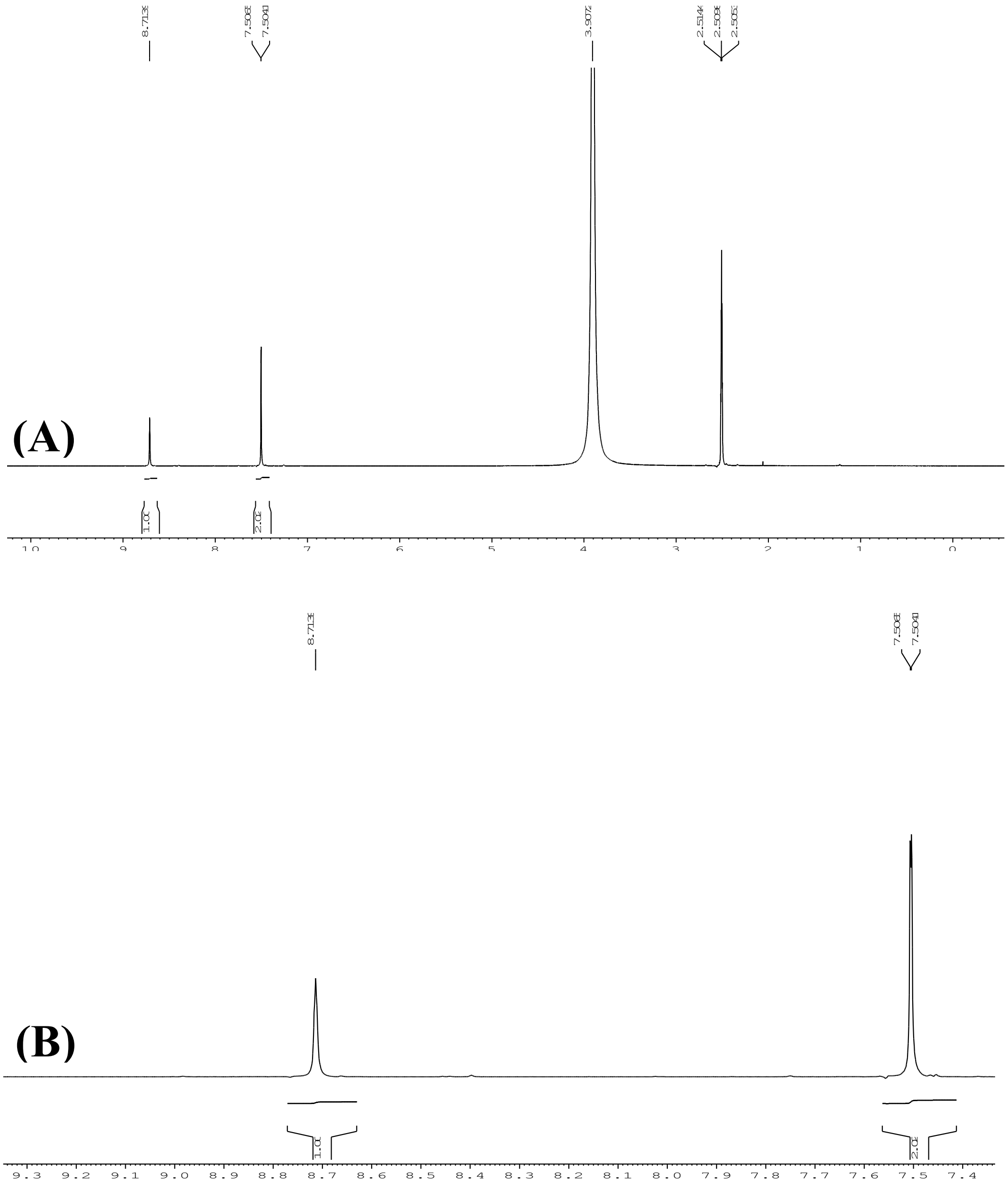


Figure S4: (A) and (B) are the ^{1}HNMR Spectrum of Charge Transfer Complex $[(IZ)^+(OX)^-]$.

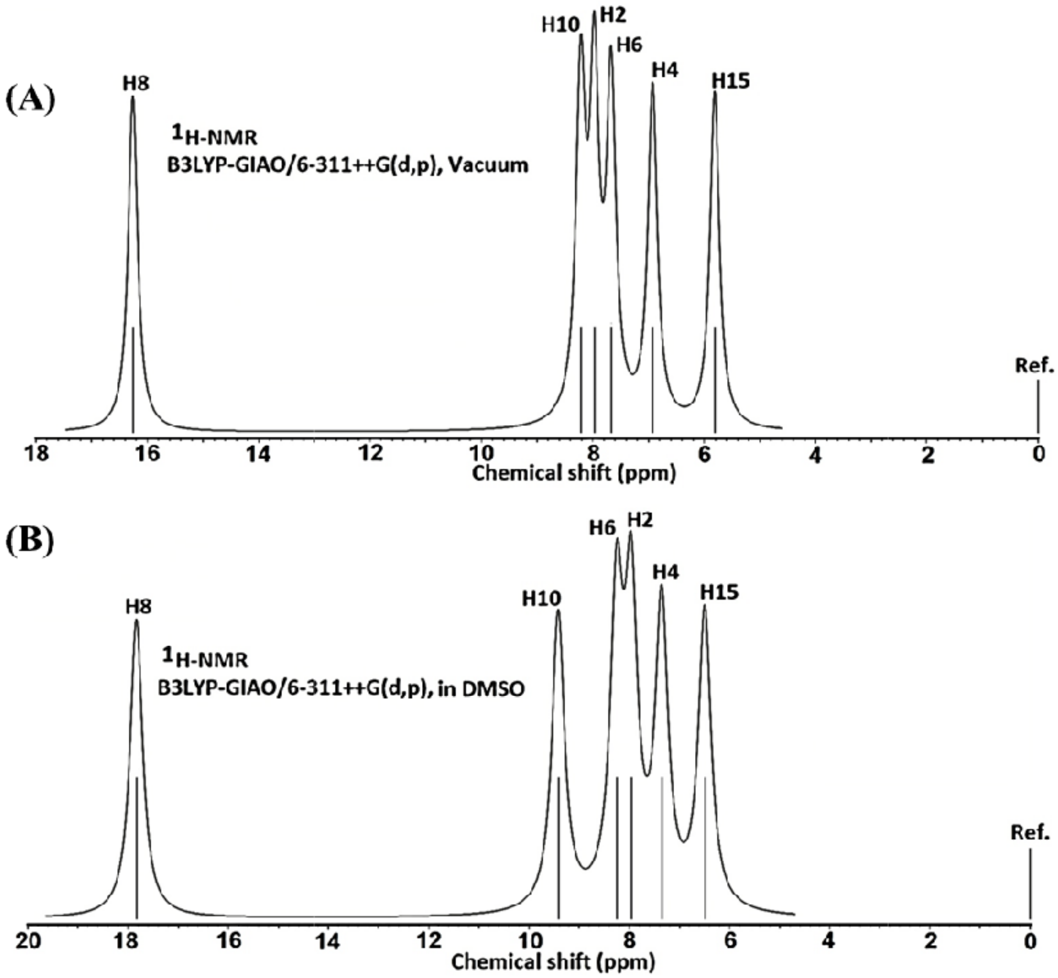


Figure S5: Simulated NMR spectra of [(IZ)$^+$(OX)$^-$] in (A) Vacuum and (B) DMSO.

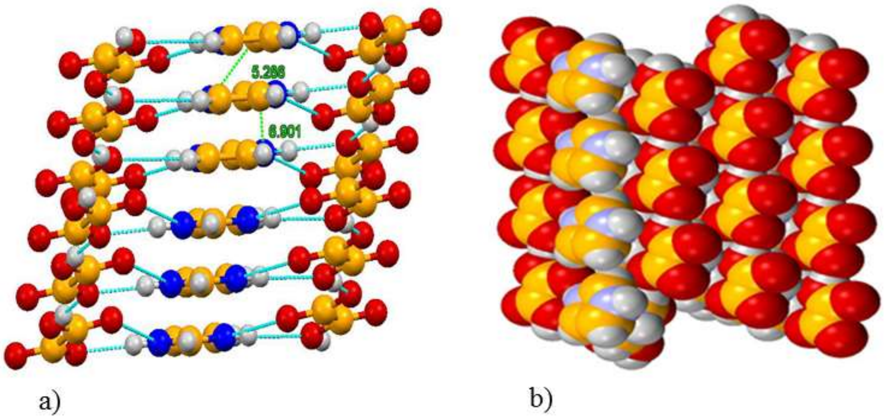


Figure S6: (a) Packing structure of complex [(IZ)$^{+}$(OX)$^{-}$] showing mean interplanar distance between N2C3 and N1C2 are 5.286 and 6.901**(b)** CPK representation of packing structure of crystal.

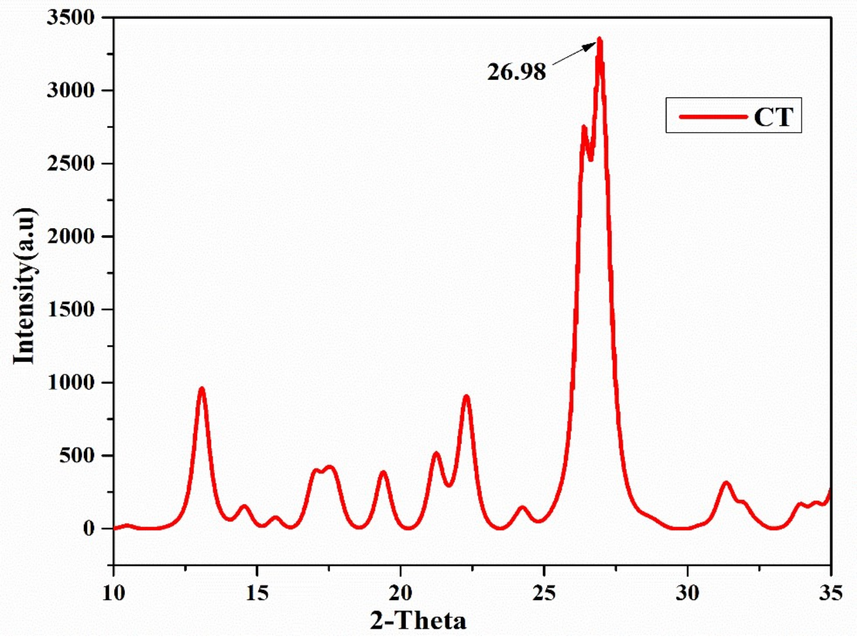


Figure S7: PXRD pattern of the CT complex.

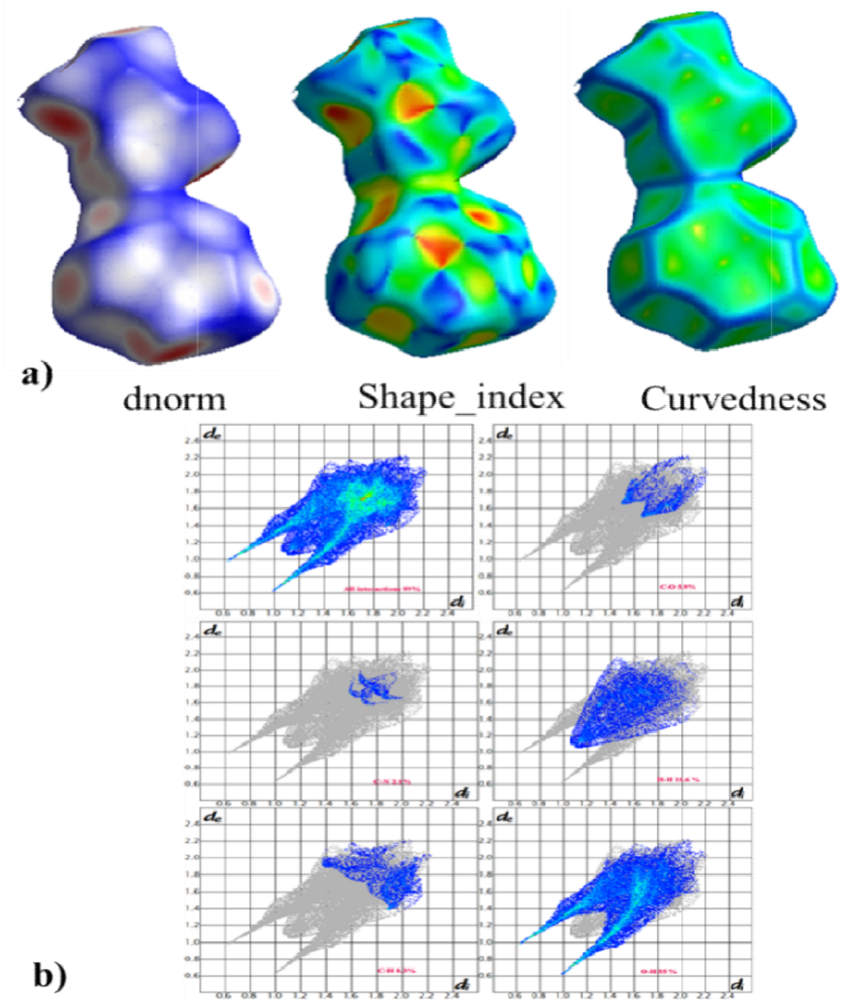


Figure S8: (a) Hirshfeld Surface (**b**) 2D fingerprint plots of the CT complex.

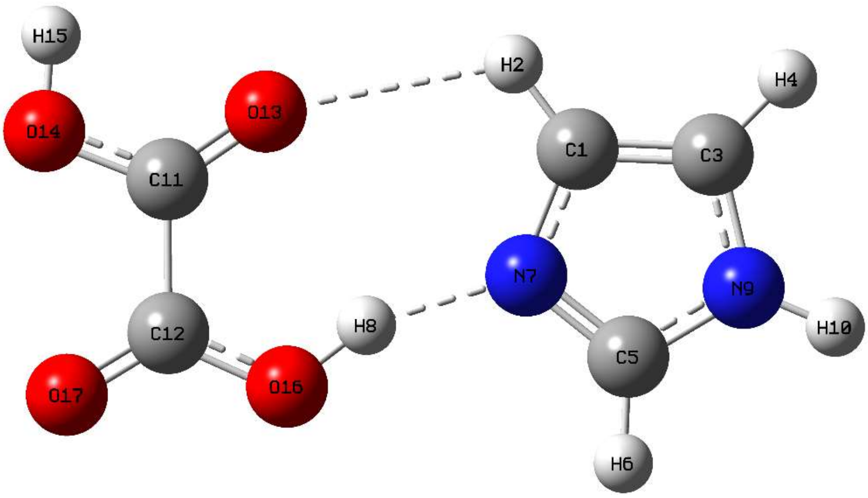


Figure S9: Energy minimized charge transfer complex with atom numbering.

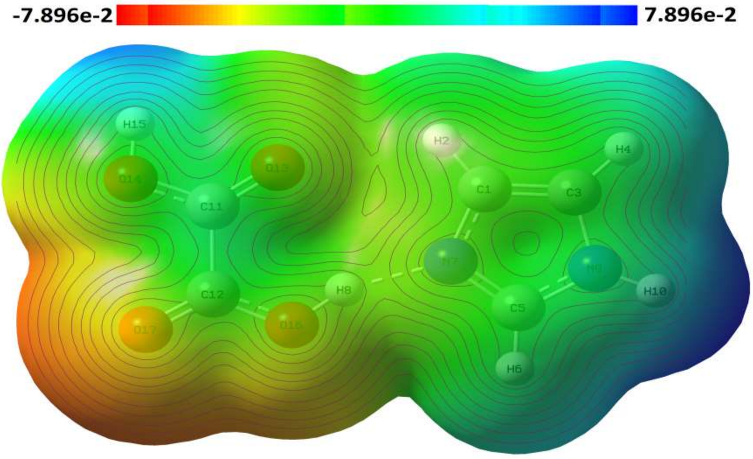
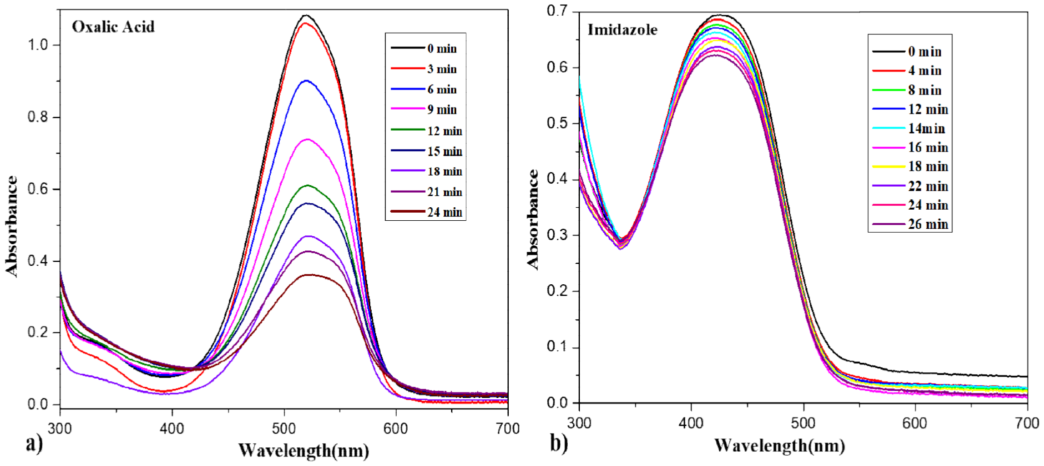


Figure S10: Molecular electrostatic potential map.



FigureS11: Degradation of the MR in the presence of acceptor **a)**Oxalic acid and donor **b)** Imidazole.

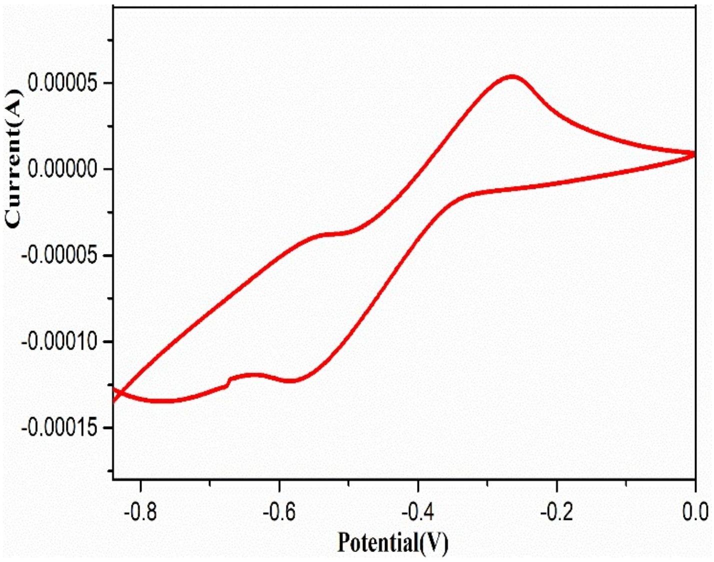


Figure S12: Cyclic Voltammogram of the prepared sample.

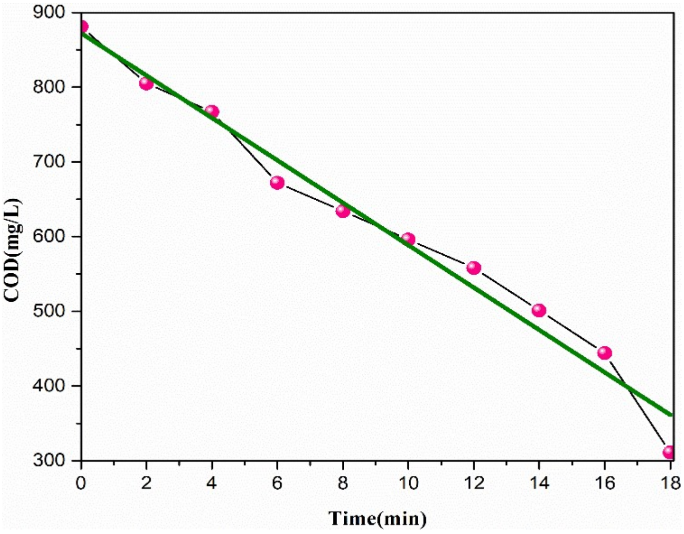


Figure S13: Rate of mineralization as function of time during degradation of methyl red under UV light.

Table S1: Ultraviolet spectral characteristic of complex

	λobs. (nm)	**B3LYP/6-311++G(d,p)/IEF-PCM**				
		E (eV)	**λmax (nm)**	***f***	**epsilon**	**composition**
Ethanol	204.2	5.7	215.4	0.0139	21106.8	H-3→LUMO (97%)
	228.4	5.6	219.9	0.0592	89893.8	H-2→LUMO (94%)
Acetonitrile	205.8	5.7	216.1	0.0195	29509.8	H-3→LUMO (95%)
	218.8	5.6	219.8	0.0531	80357.3	H-2→LUMO (93%)
DMSO	213.9	5.7	216.5	0.0229	34627.9	H-3→LUMO (93%)
	245.2	5.6	219.9	0.0517	78177.5	H-2→LUMO (91%)
Vacuum		6.2	200.5	0.0238	35089.0	H-5→L (44%), H-3 → L (45%)
		6.2	203.1	0.0009	1326.9	H-1→L+1 (92%)
		5.5	224.0	0.0011	1621.7	H-5→L (23%), H-3 →L (44%), H-2 →L (30%)
		5.5	224.7	0.0002	294.9	H→L+1 (99%)
		4.9	253.4	0.0002	294.9	H→L (99%)
		4.1	304.1	0.0002	294.9	H-1→L (98%)

Abbreviation used: H-HOMO, L-LUMO, E- excitation energy, *f*- oscillator strength

Table S2: Theoretical and observed ^{1}H-NMR chemical shifts (δ/ppm) of compound

Proton NMR			
Atom[a]	$\delta_{exp.}$	$\delta_{calc.}$	
		Solvent	**Vacuum**
H8		17.8277	16.2535
H10	9.0165	9.4102	8.2107
H6	9.0057	8.2438	7.6643
H2	8.8994	7.9558	7.9673
H4	8.8940	7.3468	6.9211
H15	5.7483	6.4877	5.8065

Table S3: Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for complex. Ueq is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
C1	2571(4)	662.8(13)	1741(4)	13.7(6)
C2	3068(4)	-83.9(13)	2099(4)	13.4(6)
C3	6534(4)	534.0(13)	2782(4)	13.5(6)
C4	-1467(4)	2687.2(13)	1701(4)	10.7(5)
C5	-3944(4)	3057.6(13)	1677(4)	11.5(5)
N1	4764(4)	1035.3(11)	2172(3)	13.0(5)
N2	5558(4)	-152.5(11)	2738(3)	12.6(5)
O1	-1197(3)	2004.5(9)	1723(3)	17.7(5)
O2	228(3)	3196.0(9)	1699(3)	15.3(4)
O3	-5623(3)	2590.3(9)	1702(3)	14.8(4)
O4	-4103(3)	3763.5(9)	1636(3)	15.2(4)

Table S4: Anisotropic Displacement Parameters (Å^2×10^3) for ka1_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{12}**	**U_{13}**	**U_{23}**
C1	10.5(12)	15.6(13)	15.8(13)	1.7(10)	4.7(10)	0.2(10)
C2	10.5(12)	12.9(13)	16.5(14)	-0.8(10)	3.2(10)	-1.0(10)
C3	8.5(12)	15.2(13)	17.1(14)	-0.4(10)	4.4(10)	0.3(10)
C4	11.7(12)	11.7(13)	8.7(12)	-0.6(10)	2.7(10)	-0.1(10)
C5	10.7(12)	12.2(13)	10.8(13)	-0.6(10)	1.6(10)	-0.7(10)
N1	16.8(11)	7.9(10)	15.9(11)	-1.6(9)	7.2(9)	-1.1(8)
N2	14.0(11)	8.5(10)	15.4(11)	1.8(8)	4.3(9)	1.3(8)
O1	13.9(9)	9.9(9)	31.3(11)	2.4(7)	9.7(8)	1.3(8)
O2	9.3(9)	10.3(8)	27.8(10)	1.3(7)	7.4(8)	1.4(7)
O3	9.7(9)	11.2(9)	24.1(10)	-0.3(7)	5.7(7)	0.6(7)
O4	10.7(9)	9.4(9)	25.7(10)	0.3(7)	5.2(8)	-0.8(7)

Table S5: Bond Lengths

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.347(3)	C4	C5	1.549(3)
C1	N1	1.368(3)	C4	O1	1.207(3)
C2	N2	1.368(3)	C4	O2	1.315(3)
C3	N1	1.314(3)	C5	O3	1.263(3)
C3	N2	1.323(3)	C5	O4	1.241(3)

Table S6: Bond Angles

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	C1	C2	107.0(2)	O3	C5	C4	114.68(19)
N2	C2	C1	106.8(2)	O4	C5	C4	118.6(2)
N2	C3	N1	108.7(2)	O4	C5	O3	126.7(2)
O1	C4	C5	121.9(2)	C3	N1	C1	108.8(2)
O2	C4	C5	112.44(19)	C3	N2	C2	108.64(19)

Table S7: Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3)

Atom	***x***	***y***	***z***	**U(eq)**
H1	1028(4)	883.2(13)	1287(4)	16.5(7)
H2	1936(4)	-477.0(13)	1942(4)	16.1(7)
H3	8197(4)	643.5(13)	3178(4)	16.2(7)
H1a	4953(4)	1518.4(11)	2063(3)	15.6(6)
H2a	6357(4)	-571.8(11)	3058(3)	15.1(6)
H2b	1504(14)	2978.2(9)	1710(40)	23.0(7)

Table S8: Comparison of Mullikan's atomic charges (*e*) of complex and its constituents

Atom	B3LYP/6-311++G(d,p)		
	Imidazole	**Oxalic acid**	**complex**
C1	-0.107		0.101
H2	0.151		0.185
C3	-0.191		-0.389
H4	0.134		0.159
C5	-0.069		-0.083
H6	0.157		0.172
N7	-0.207		-0.429
H8		0.251	0.635
N9	-0.164		-0.139
H10	0.297		0.330
C11		0.149	0.093
C12		0.126	0.145
O13		-0.298	-0.308
O14		-0.135	-0.118
H15		0.295	0.289
O16		-0.147	-0.378
O17		-0.242	-0.264

Table S9: Various other theoretical molecular parameters of complex and its constituents.

Parameters	**B3LYP/6-311++G(d,p)**		
	Imidazole	**Oxalic acid**	**complex**
Minimum SCF energy (kcal/mol)	-141994.6343	-237481.3612	-379486.8433
Binding energy (kcal/mol)			10.848
Polarizability	46.578990	37.099208	86.820472
Zero point vibrational energy (kcal/mol)	44.44928	30.79491	75.73703
Total thermal energy (kcal/mol)	46.819	34.200	82.555
Molar heat capacity at const. volume, Cv (cal mol–1 K–1)	13.475	18.371	36.693
Total entropy, S (cal mol1 K1)	65.234	75.004	110.140
Field independent dipole moment (Debye)			
µx	1.5671	-2.9922	7.3867
µy	3.4963	1.4090	2.7540
µz	0.0001	0.0000	0.0002
µtotal	3.8314	3.3074	7.8834
Frontier MO Energies (eV)			
LUMO	-0.51	-2.69	-1.78
HOMO	-6.56	-8.34	-7.16
Gap (LUMO-HOMO)	6.04	5.65	5.38
Global reactivity descriptors			
Hardness	3.025	2.825	2.690
Chemical potential	-3.535	-5.515	-4.470
Electron affinity	0.510	2.690	1.780
Electrophilicity	2.065	5.383	3.714
Electronegativity	3.535	5.515	4.470
Ionization potential	6.560	8.340	7.160
Softness	0.165	0.177	0.186

Table S10: Reduction of COD of MR

Time (min)	COD before irradiation (mg L^{-1})	COD after irradiation (mg L^{-1})	% degradation
0	881	881	0
2	881	805	8.62
4	881	767	12.93
6	881	672	23.72
8	881	634	28.03
10	881	596	32.34
12	881	558	36.66
14	881	501	43.13
16	881	444	46.60
18	881	311	64.69