Supporting Information

Unveiling the effects of *in situ* generated arene anion radical and imine radical on catecholase like activity: A DFT supported experimental investigation

Sanchari Dasgupta,[a] Jaydeep Adhikary,[a] Sanjib Giri, [a] Antonio Bauza, [b]Antonio Frontera, [b] and Debasis Das*[,a]

[a]Department of Chemistry, University of Calcutta, 92, A. P. C. Road, Kolkata – 700009, India.

[b]Departament de Química, Universitat de les Illes Balears, Crta. de Valldemossa km 7.5, 07122, Palma (Baleares), Spain

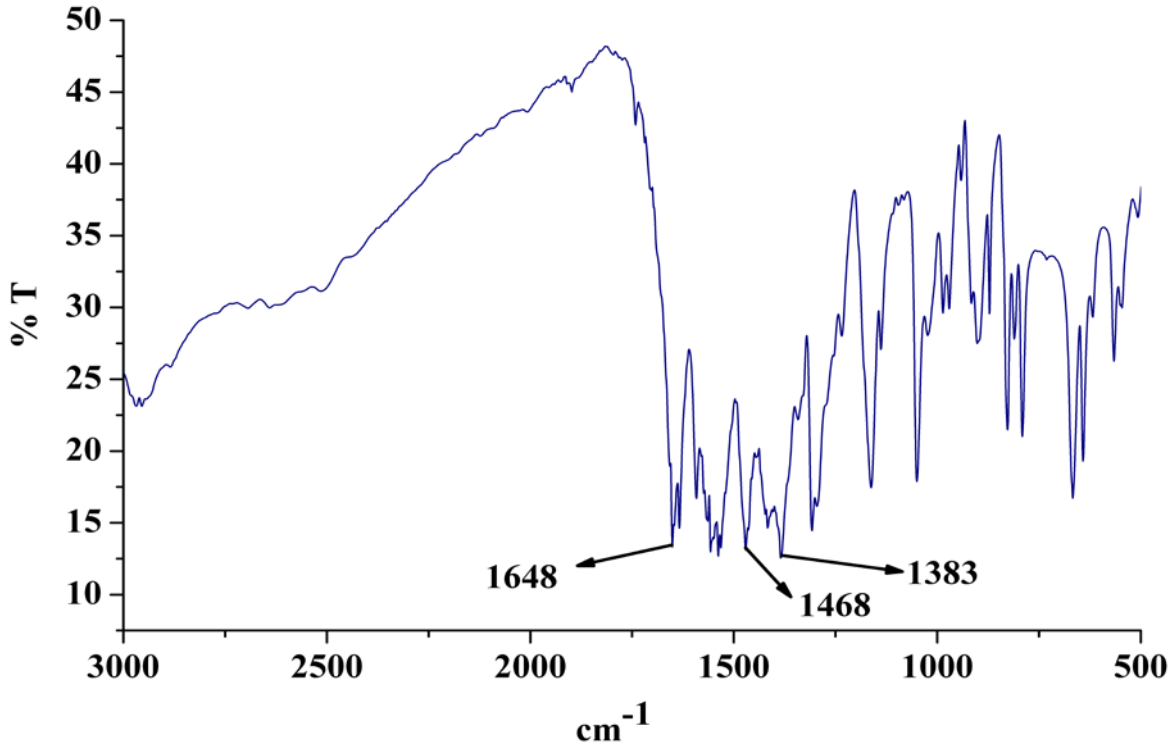


Fig. S1 FTIR spectrum of complex **1**.

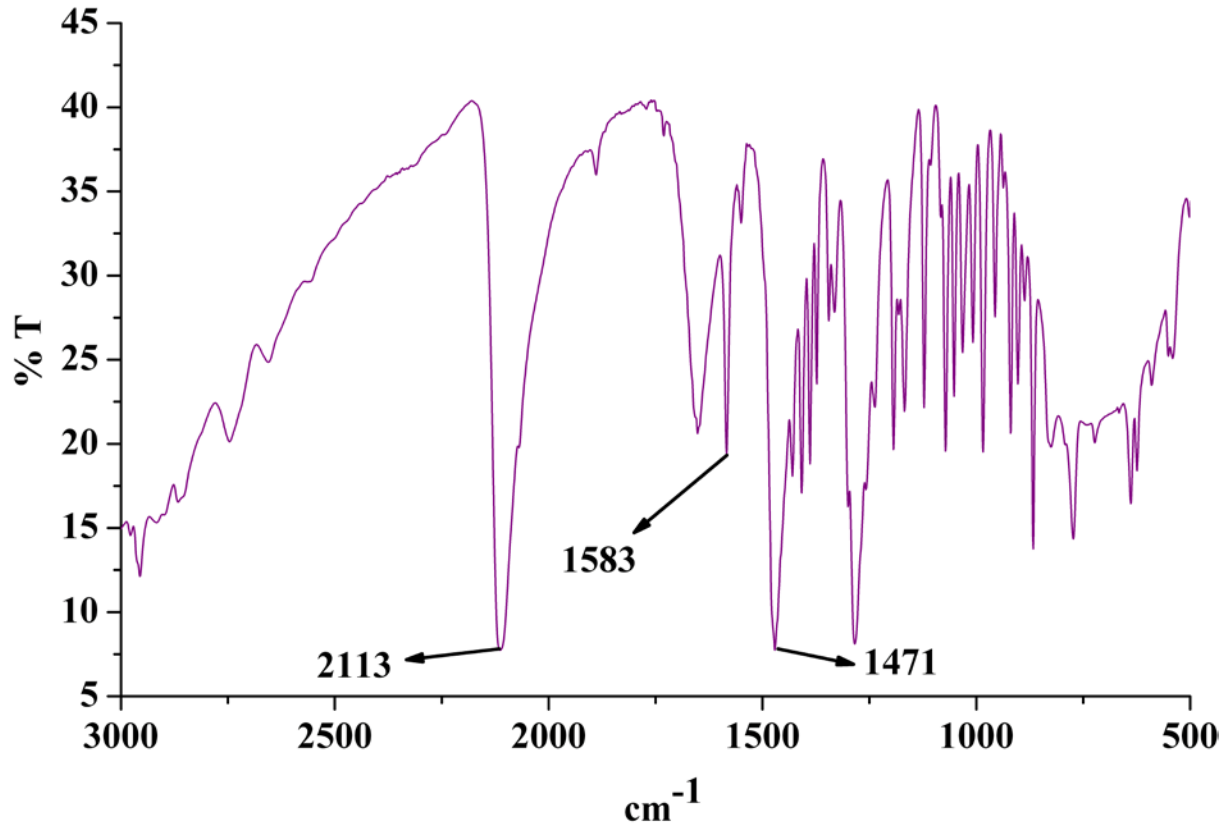
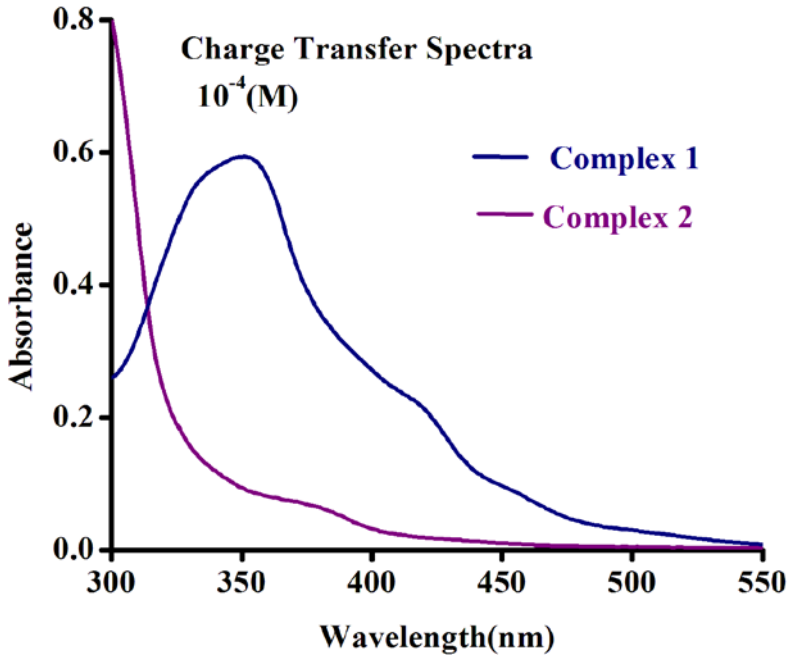
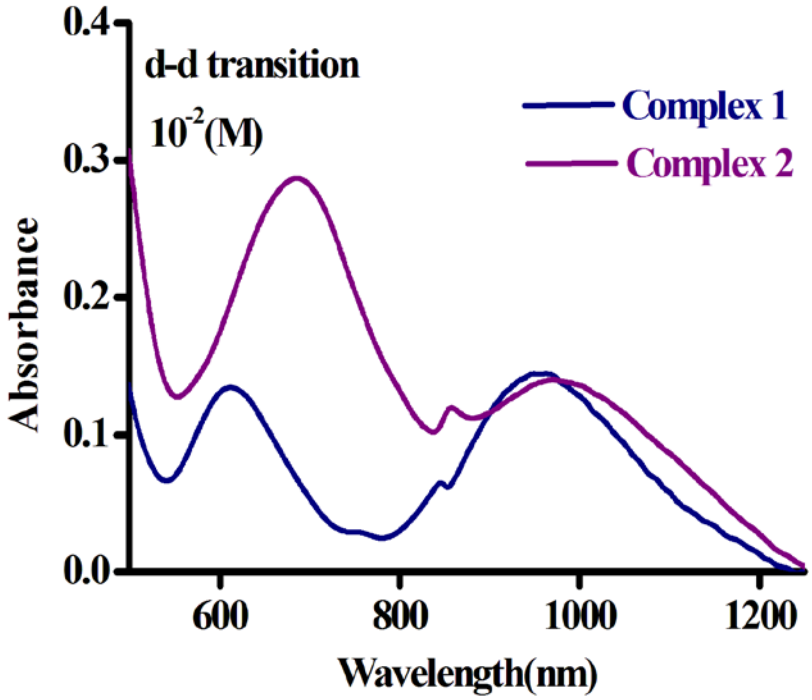


Fig. S2 FTIR spectrum of complex **2**



(a)



(b)

Fig. S3 UV-Vis spectra of complexes.

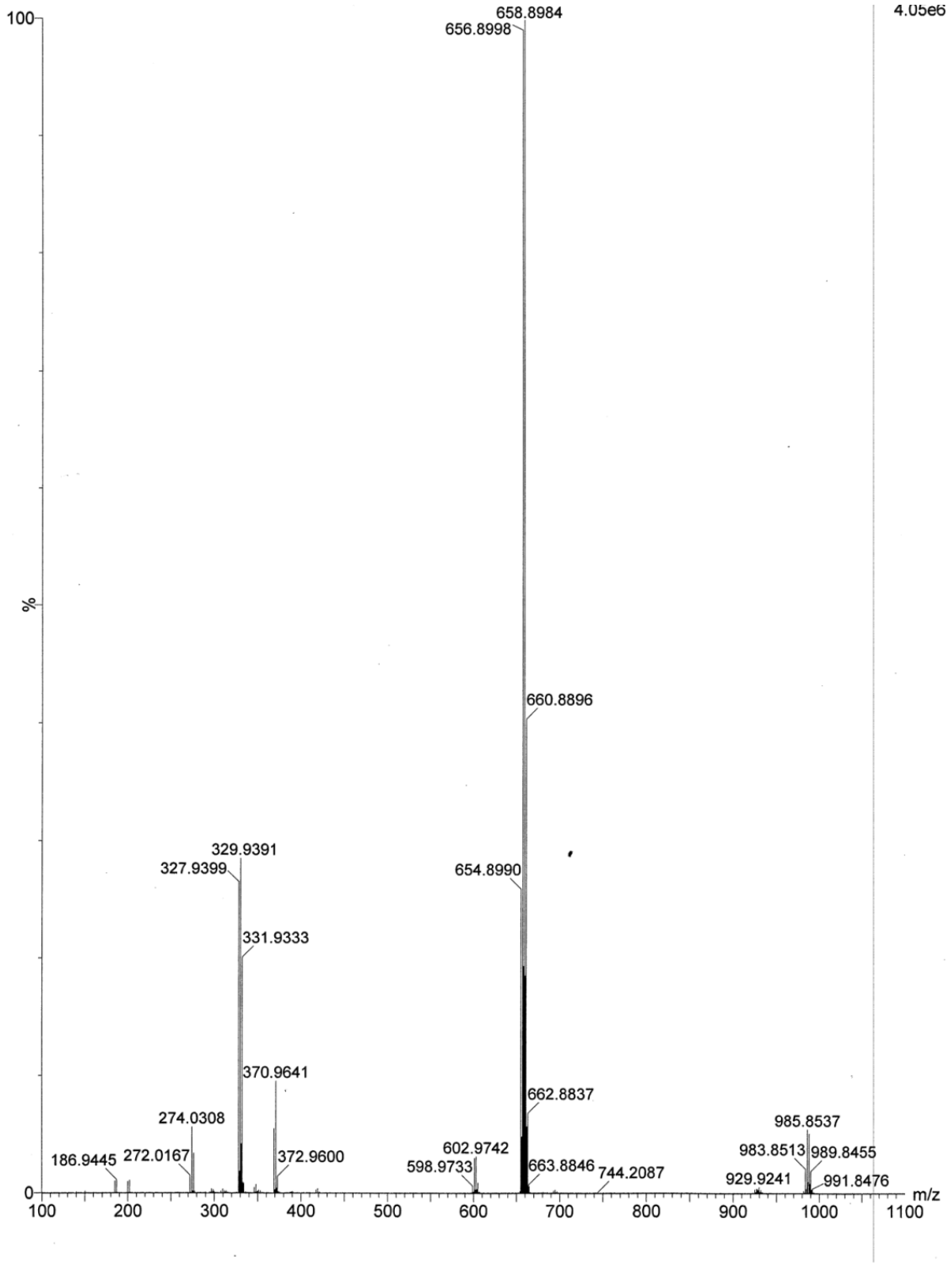


Fig.S4 ESI-MS spectrum of complex **1**.

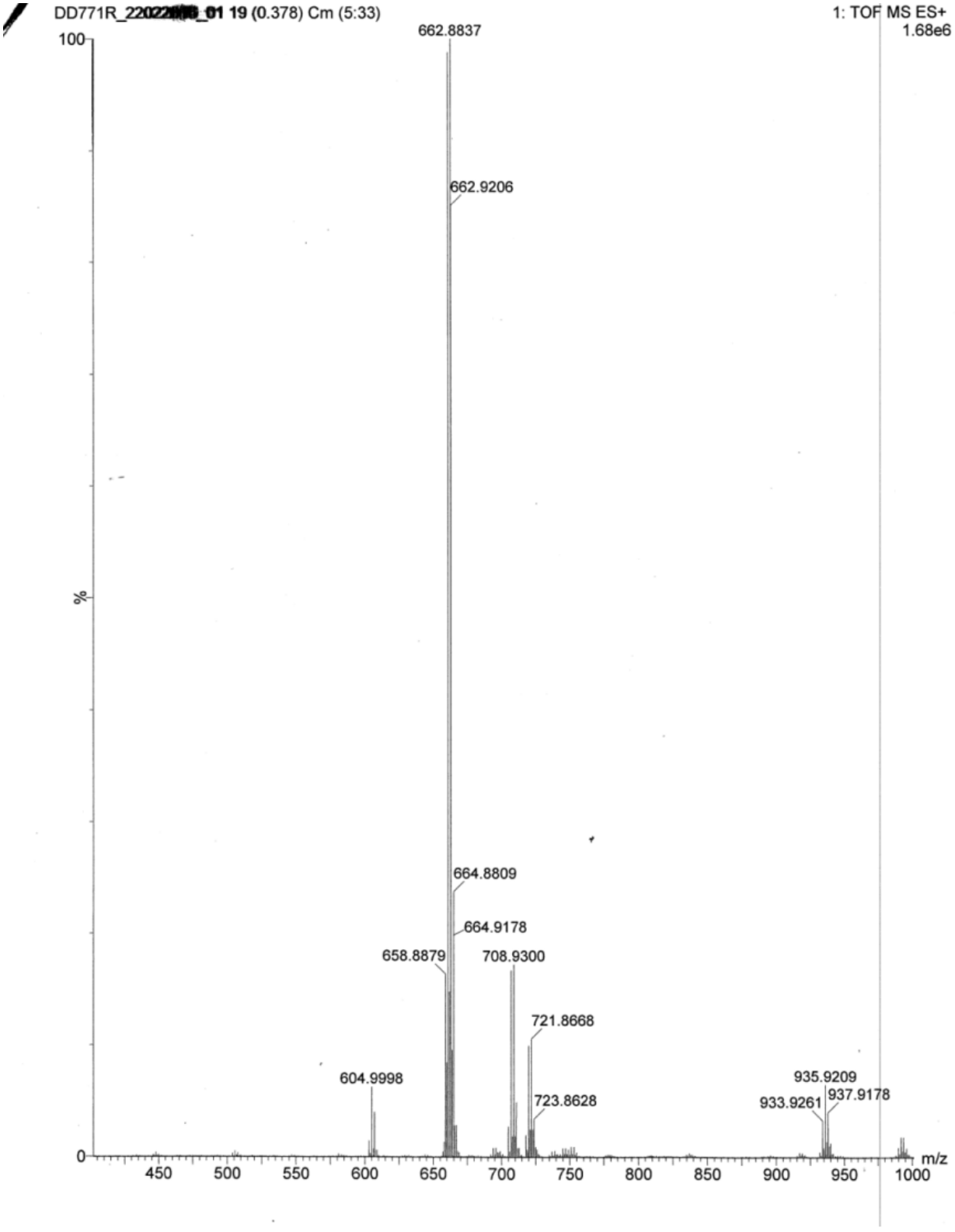
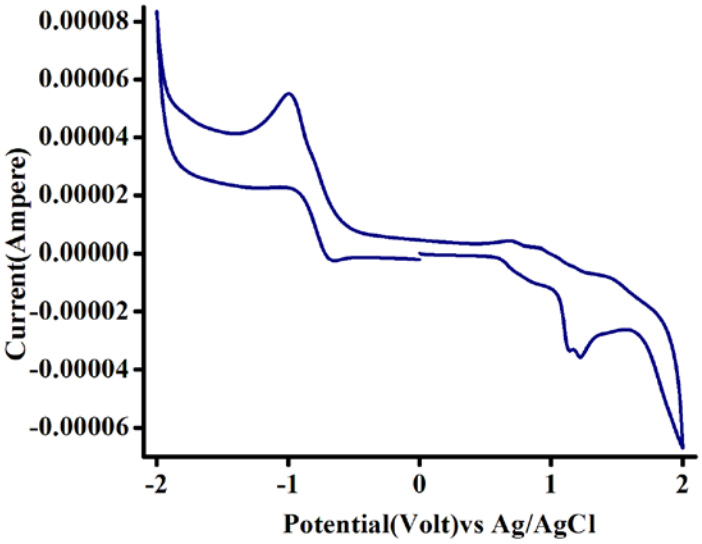
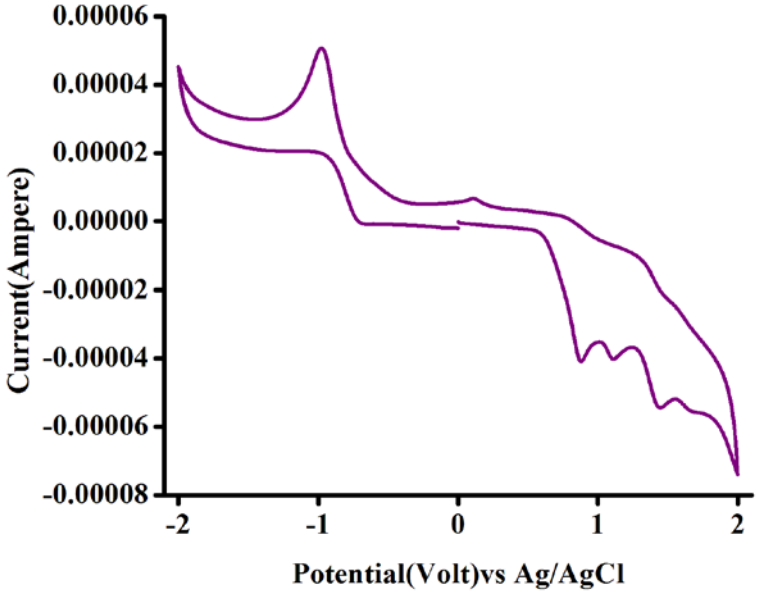


Fig. S5 ESI-MS spectrum of complex **2**.



(a)



(b)

Fig. S6 Cyclic voltammetry of (a) complex **1** and (b) complex **2**

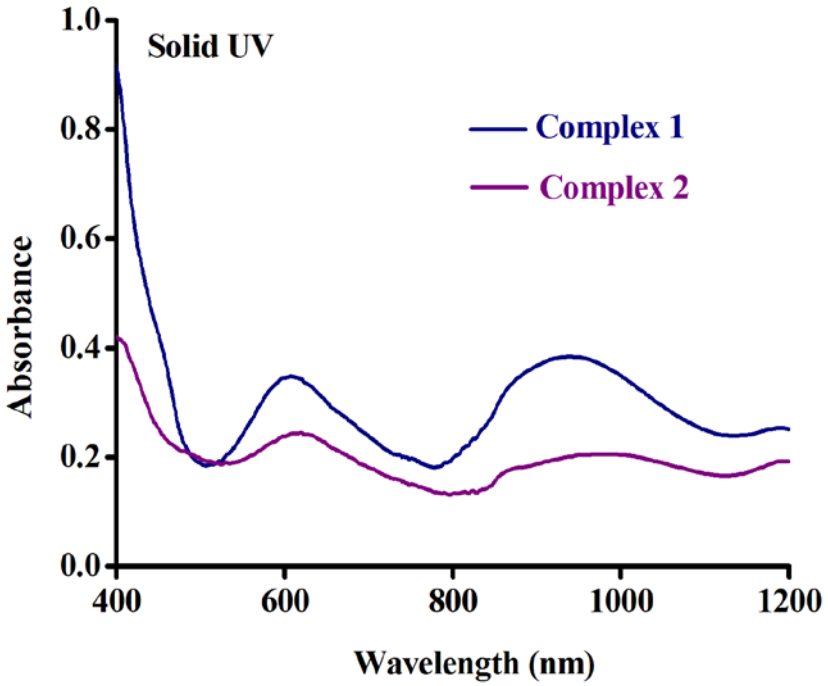


Fig. S7 Solid UV-Vis spectra of complexes.

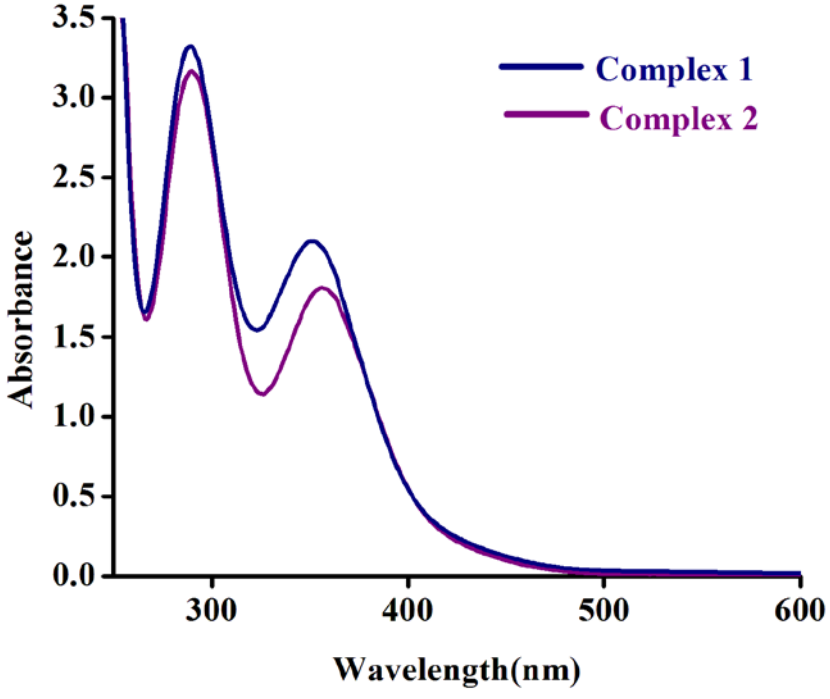
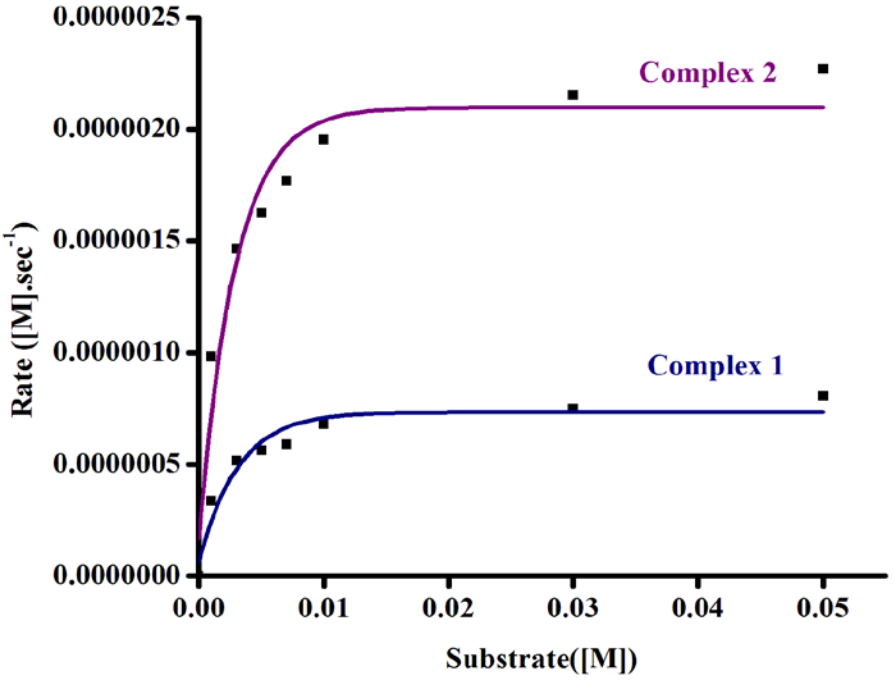
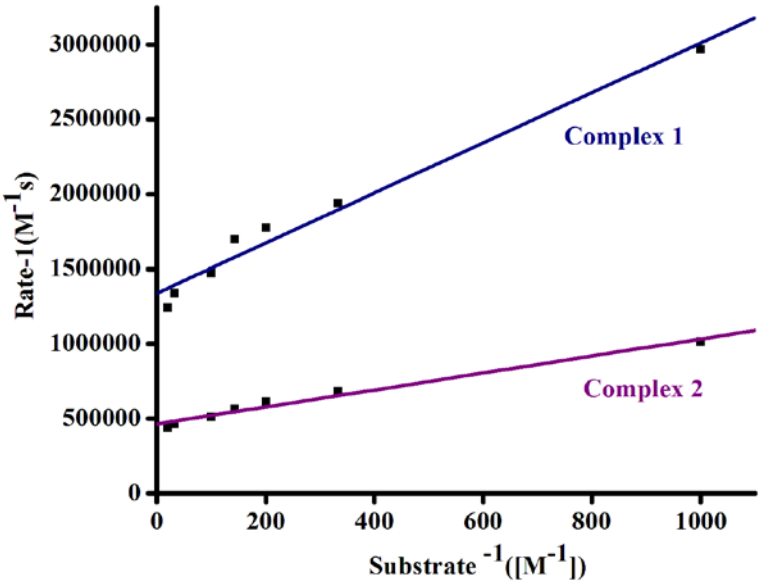


Fig. S8 Detection of H_2O_2 formation during oxidation of 3,5-DTBC observed spectrophotometrically



(a)



(b)

Fig. S9 (a) Dependence of rate of reaction on substrate concentration for Complex **1** and **2**(100 μM) and (b) Lineweaver−Burk plots for Complex **1** and **2** at 25°C in Acetonitrile (100 μM) for oxidation of Catechol

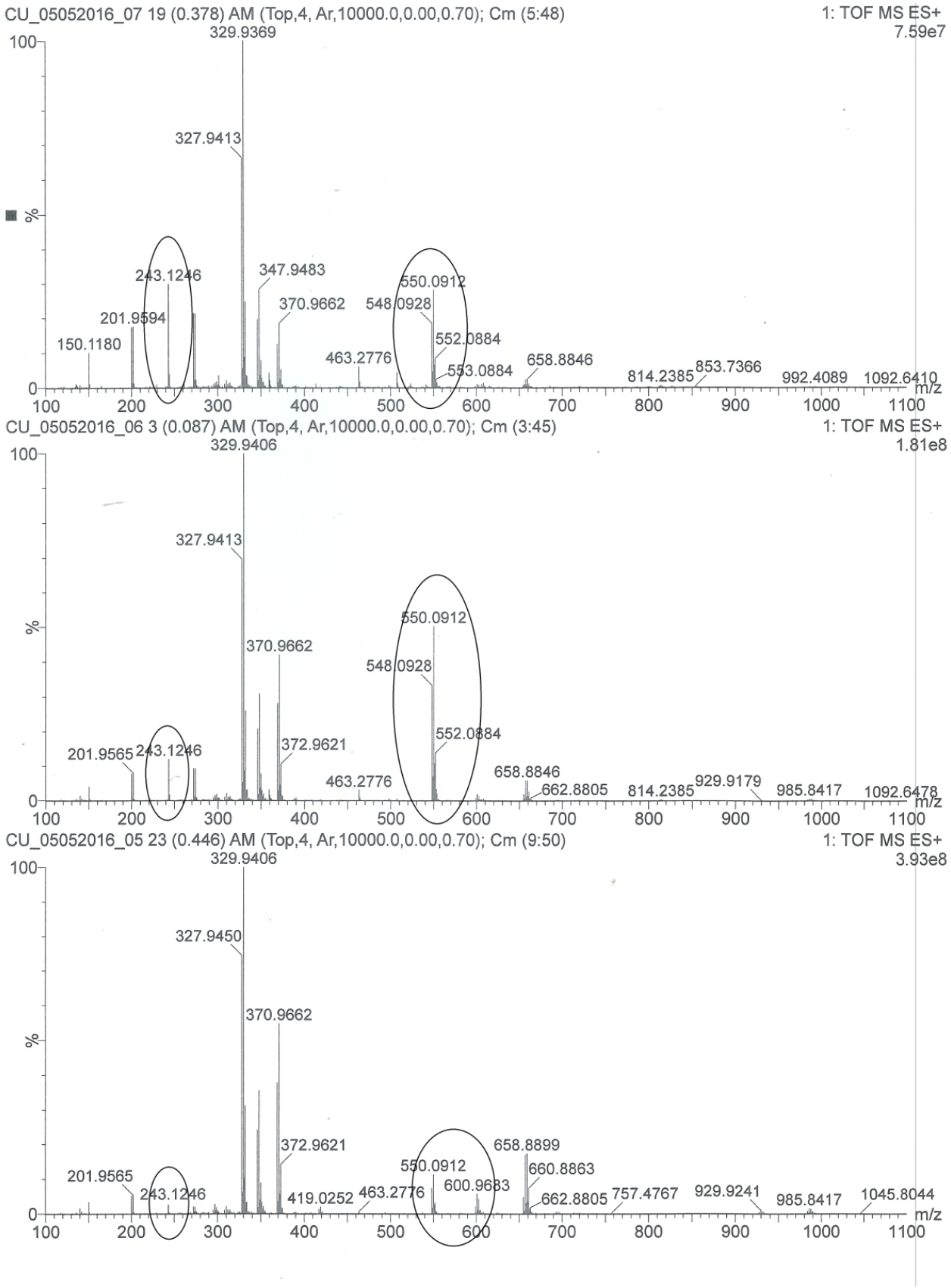


Fig. S10 ESI-MS spectra of reaction mixture of complex **1** and 3,5-DTBC recorded at different time interval.

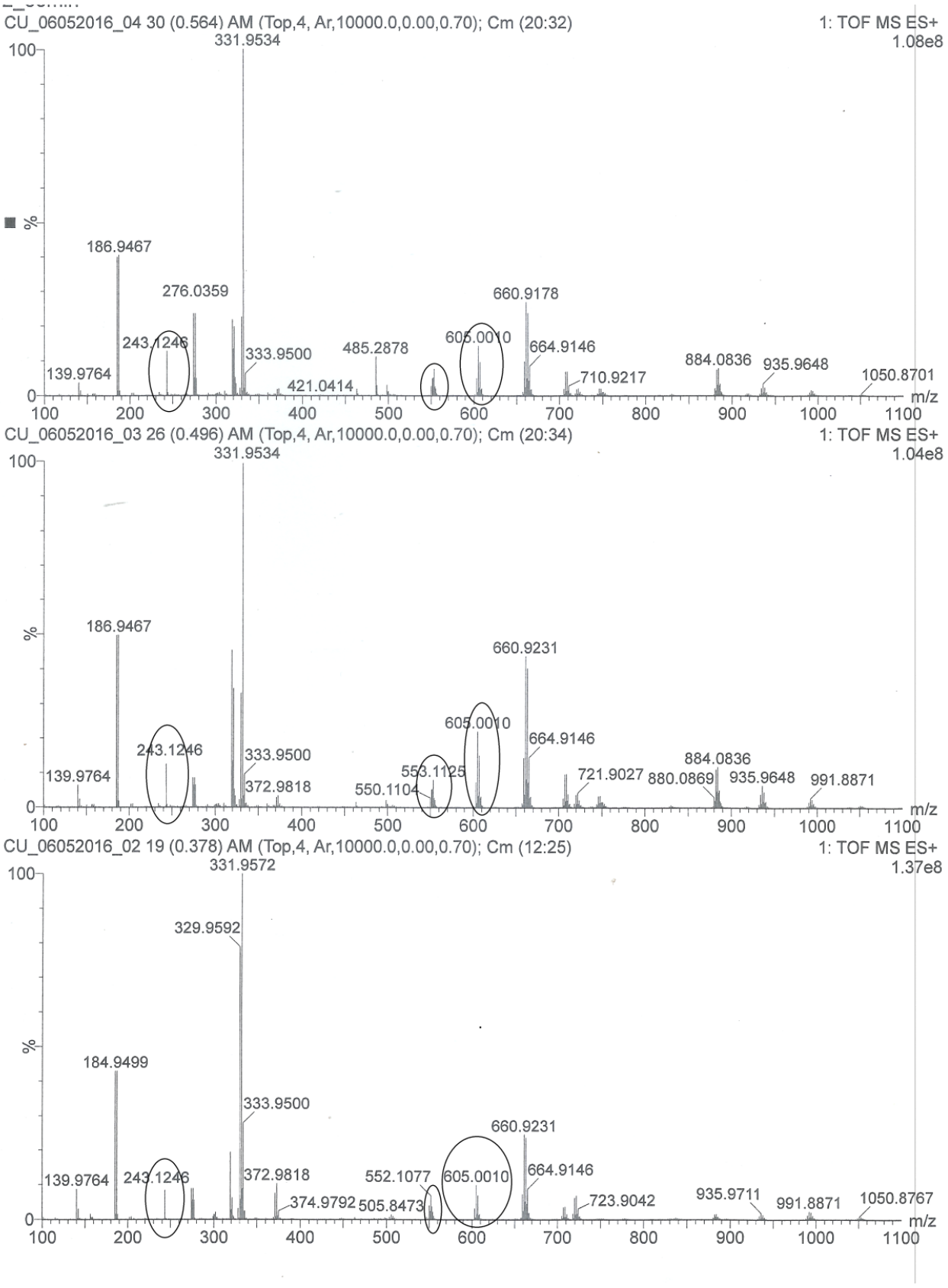
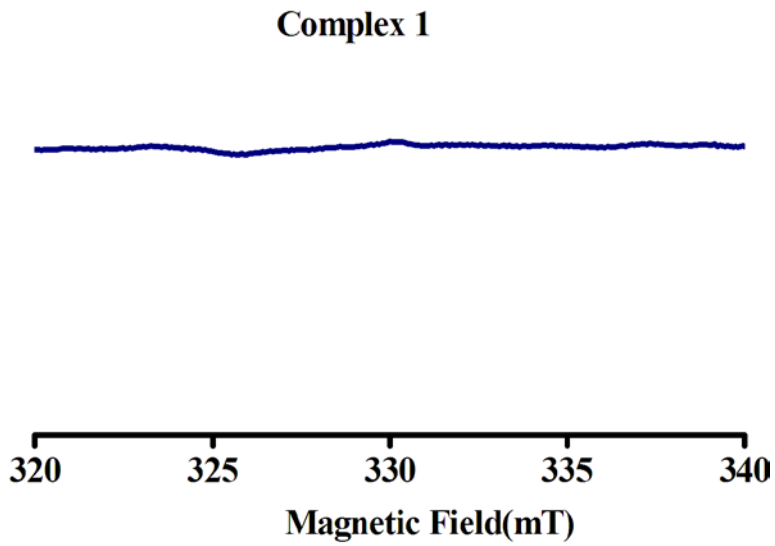
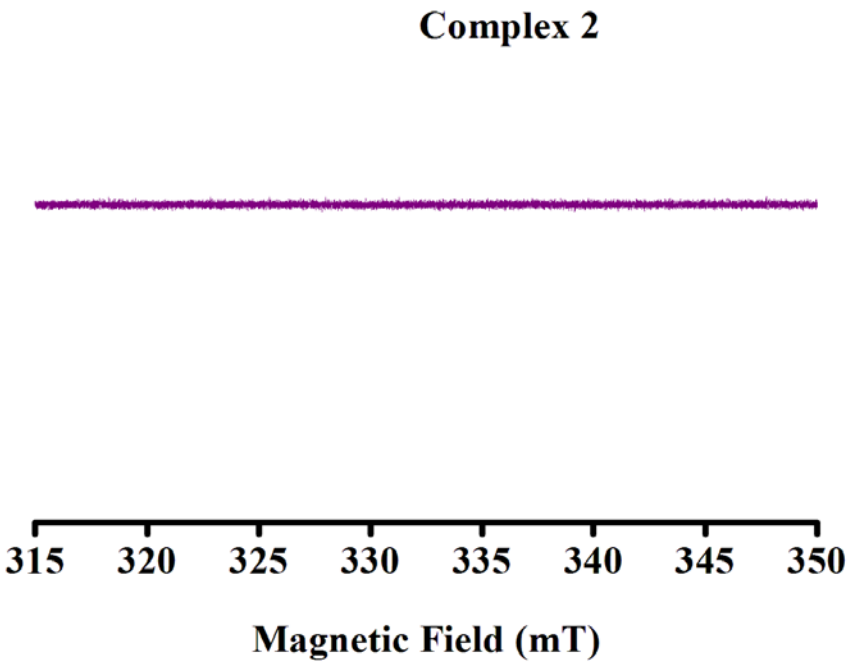


Fig. S11 ESI-MS spectra of reaction mixture of complex **2** and 3,5-DTBC recorded at different time interval.



(a)



(b)

Fig. S12 EPR spectra of (a) complex **1** and (b) complex **2 in** acetonitrile medium

Table S1 Selected parameters for vertical excitation (UV-vis absorptions) of **1** and **2**. Electronic excitation energies (eV), oscillator strengths (*f*), configurations of the two lowest lying excited states of **1** and **2**; calculation of the S_0–S_n energy gaps based on optimized ground-state geometries (UV-vis absorption) (CH_3CN used as solvent)

Process	Electronic transitions	Composition	Excitation energy (λ)	Oscillator strength (f)	λ_{exp} (nm)
Complex **1**					
Absorption	$S_0 \rightarrow S_1$	HOMO → LUMO (100%)	1.4238 eV (871 nm)	0.0002	950-980
Absorption	$S_0 \rightarrow S_2$	HOMO → LUMO+1 (96%)	1.8920 eV (655 nm)	0.0045	610-690
Complex **2**					
Absorption	$S_0 \rightarrow S_1$	HOMO → LUMO (100%)	1.2853 eV (965 nm)	0.0029	950-980
Absorption	$S_0 \rightarrow S_2$	HOMO–1 → LUMO (36%) HOMO–2 → LUMO (13%) HOMO–3 → LUMO (51%)	2.0339 eV (610 nm)	0.0104	610-690

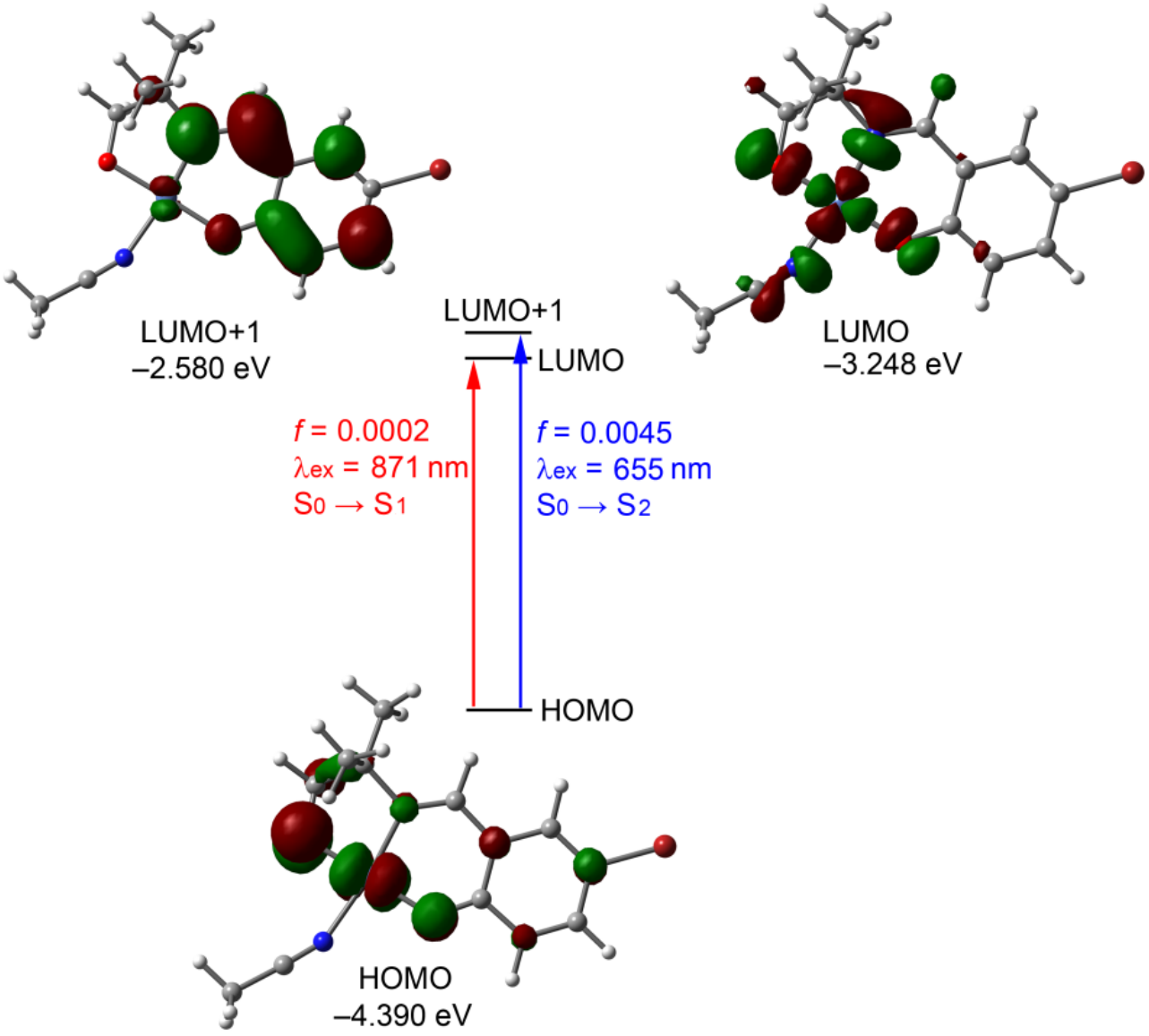


Fig. S13 Frontier molecular orbitals involved in the two lowest UV-vis absorption bands of complex **1** in acetonitrile.

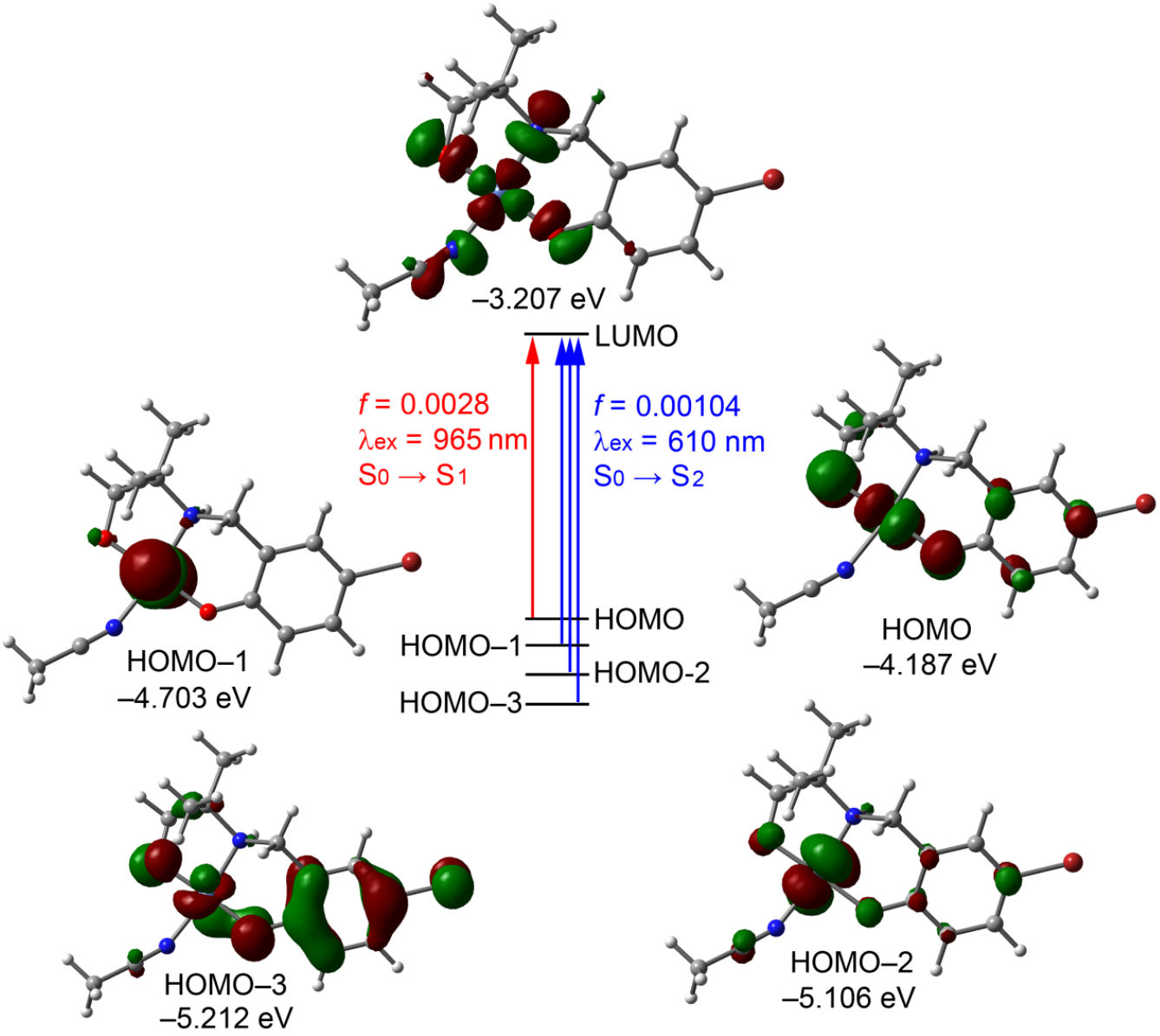


Fig. S14 Frontier molecular orbitals involved in the two lowest UV-vis absorption bands of complex **2** in acetonitrile.