

## Supporting information

### **Spectroscopic characterization and reactivity of a high valent (L)Cu(III) species supported by proline-based pseudo peptide**

Raju Eerlapally, Sikha Gupta, Ayushi Awasthi, Rakesh Kumar, and Apparao Draksharapu\*

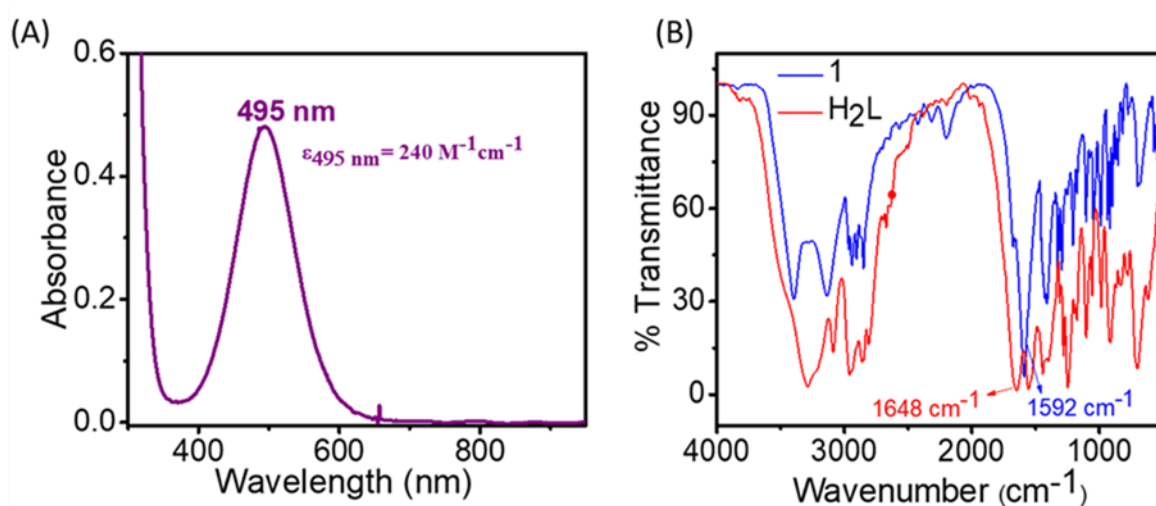
Southern Laboratories-208A, Department of Chemistry, Indian Institute of Technology  
Kanpur, Kanpur-208016, India

**Table S1:** Crystal data and structure refinement of **1**.

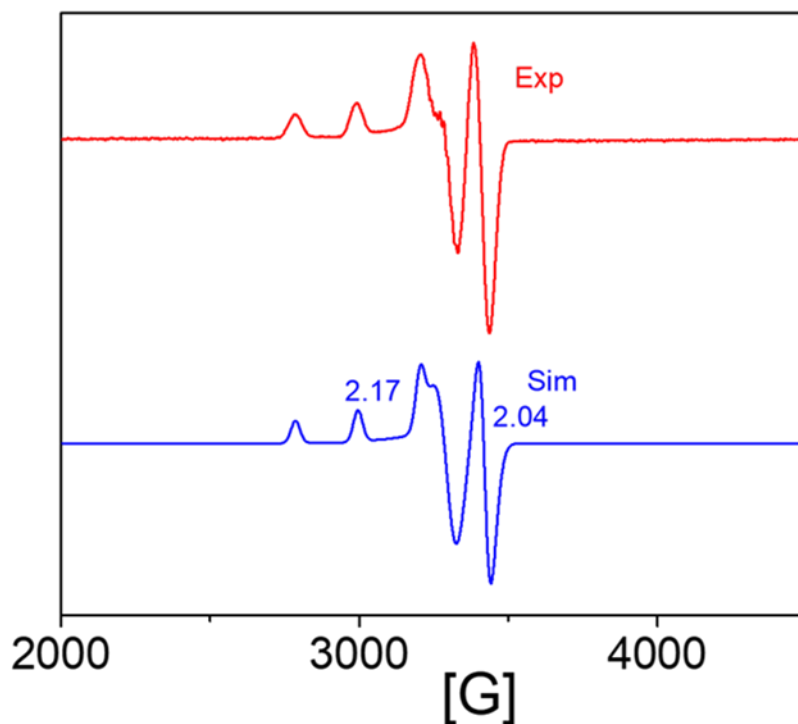
Empirical formula	C <sub>12</sub> H <sub>22</sub> CuN <sub>4</sub> O <sub>3</sub>
Formula weight	333.87
Temperature/K	100
Crystal system	trigonal
Space group	P3 <sub>2</sub> 21
a/Å	8.5368(4)
b/Å	8.5368(4)
c/Å	17.4591(11)
α/°	90
β/°	90
γ/°	120
Volume/Å <sup>3</sup>	1101.90(12)
Z	3
ρ <sub>calc</sub> /cm <sup>3</sup>	1.509
μ/mm <sup>-1</sup>	1.499
F(000)	525.0
Crystal size/mm <sup>3</sup>	0.2 × 0.18 × 0.16
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.51 to 50.014
Index ranges	-10 ≤ h ≤ 10, -10 ≤ k ≤ 10, -20 ≤ l ≤ 20
Reflections collected	13297
Independent reflections	1291 [R <sub>int</sub> = 0.0630, R <sub>sigma</sub> = 0.0281]
Data/restraints/parameters	1291/0/96
Goodness-of-fit on F <sup>2</sup>	1.109
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0196, wR <sub>2</sub> = 0.0503
Final R indexes [all data]	R <sub>1</sub> = 0.0202, wR <sub>2</sub> = 0.0510
Largest diff. peak/hole / e Å <sup>-3</sup>	0.24/-0.44
Flack parameter	0.019(19)

**Table S2:** Selected bond lengths and bond angles for **1**.

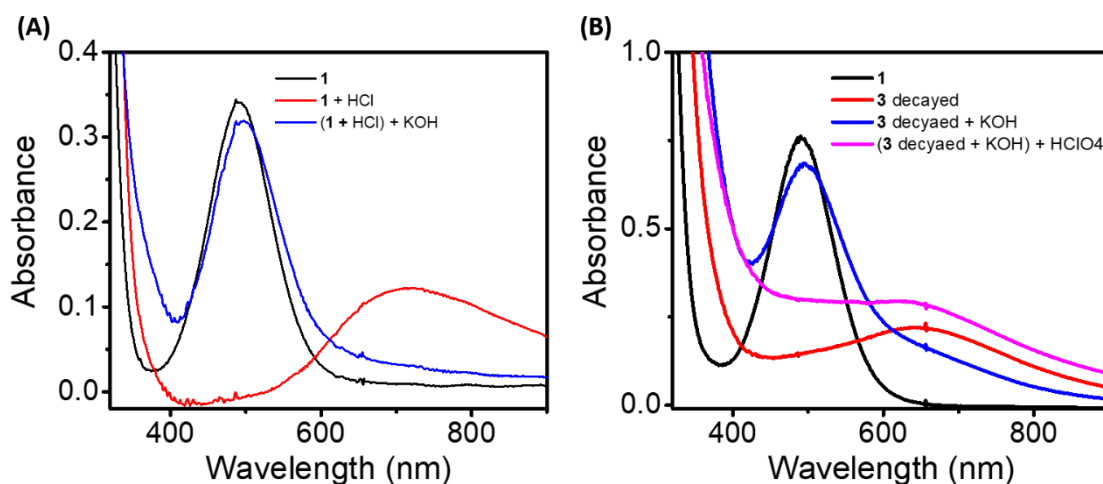
Atom	Bond length (Å) / Bond angle (°)
Cu1 -N1	1.997(2)
Cu1 -N1 <sup>1</sup>	1.997(2)
Cu1 -N2	1.895(2)
Cu1 -N2 <sup>1</sup>	1.8954(19)
N1 <sup>1</sup> -Cu1 -N1	104.66(12)
N2 <sup>1</sup> -Cu1 -N1 <sup>1</sup>	85.56(9)
N2 -Cu1 -N1	85.56(9)
N2 -Cu1 -N1 <sup>1</sup>	169.35(9)
N2 <sup>1</sup> -Cu1 -N1	169.35(9)
N2 <sup>1</sup> -Cu1 -N2	84.41(13)



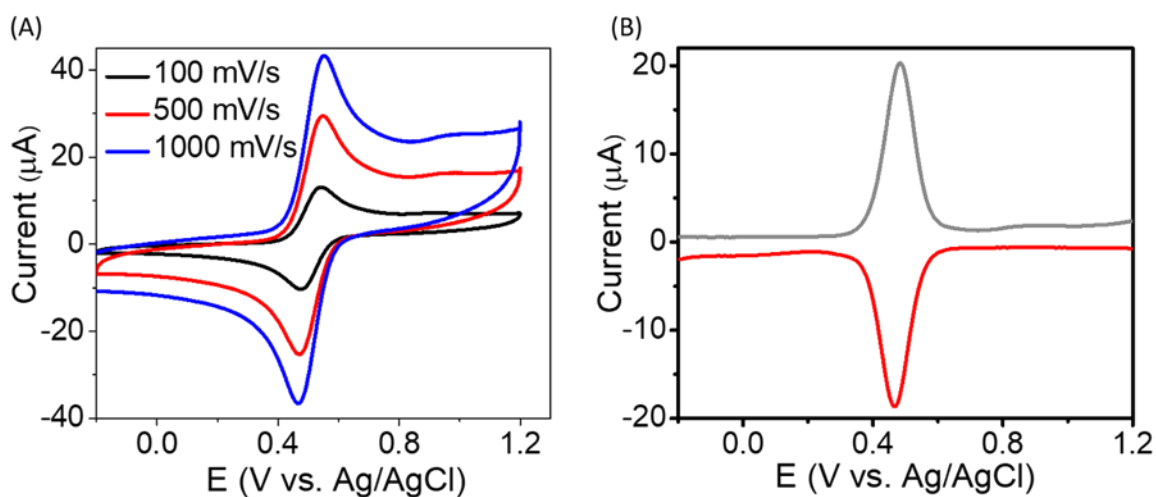
**Fig. S1.** (A) UV/Vis absorption spectrum of **1** in MeOH:CH<sub>3</sub>CN (1:20) and (B) Solid-state FT-IR spectrum of **1**.



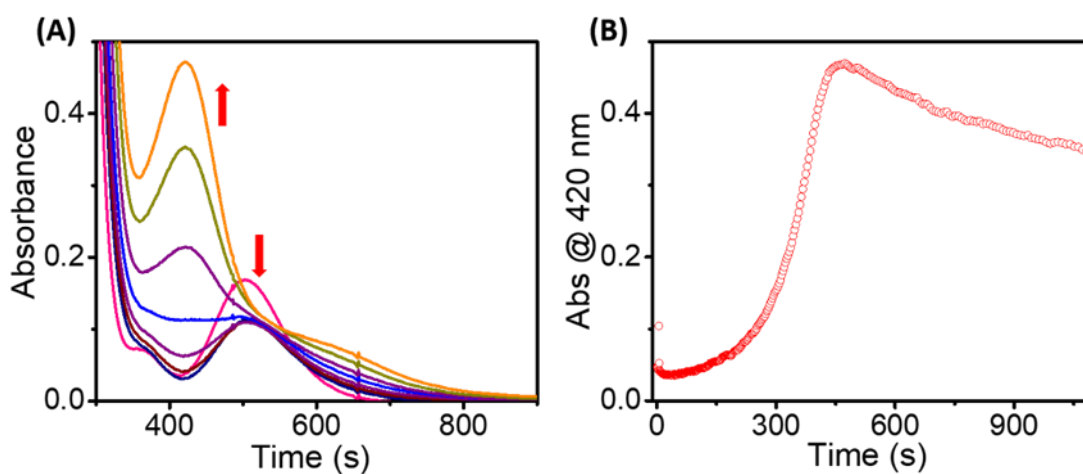
**Fig. S2.** X-band EPR (Frequency = 9.432 GHz) spectrum of **1** in MeOH:CH<sub>3</sub>CN (1:20) measured at 120 K. Red: Experimental spectrum and Blue: Simulated spectrum. Modulation amplitude 1.98 G; Modulation frequency 100 kHz, and Attenuation 18 dB. Simulated parameters:  $g_x = g_y = 2.04$ ,  $g_z = 2.17$ ;  $A_z = 980.415 \cdot 10^{-5} \text{ cm}^{-1}$ ,  $A_x = A_y = 0$ .



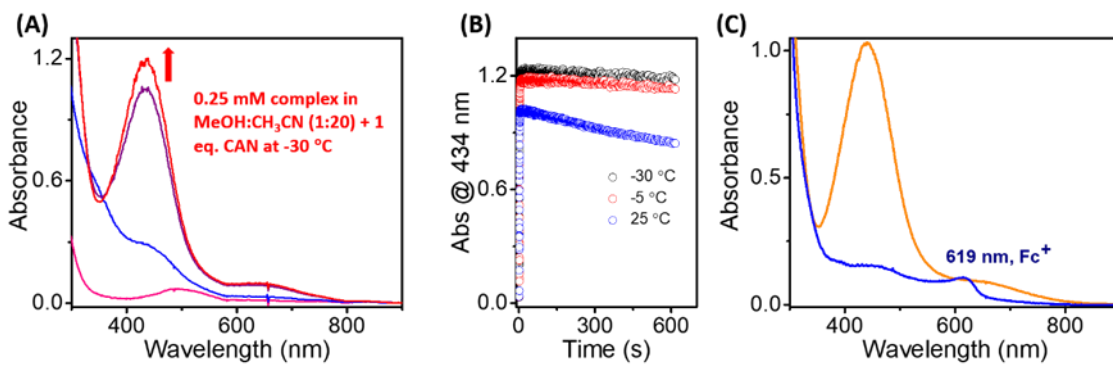
**Fig S3.** (A) UV/Vis absorption spectra showing acid-base equilibria between **1** and with a dimeric Cu(II) species. (black trace) **1** (1.5 mM) in 1:20 MeOH:CH<sub>3</sub>CN, (red trace) **1** with 2 eq. HCl and (blue trace) upon addition of 3 eq. KOH to the red trace generates **1**. (B) UV/Vis absorption spectra of **1** (black trace) (2.5 mM) in MeOH:CH<sub>3</sub>CN (1:20), red trace: decayed spectra of **3** (**3** generated upon addition of 1 eq. *m*CPBA to **1** at 25 °C), blue trace: to the decayed species of **3**, 2 eq. KOH was added, pink trace: to the blue trace 2 eq. of HClO<sub>4</sub> was added.



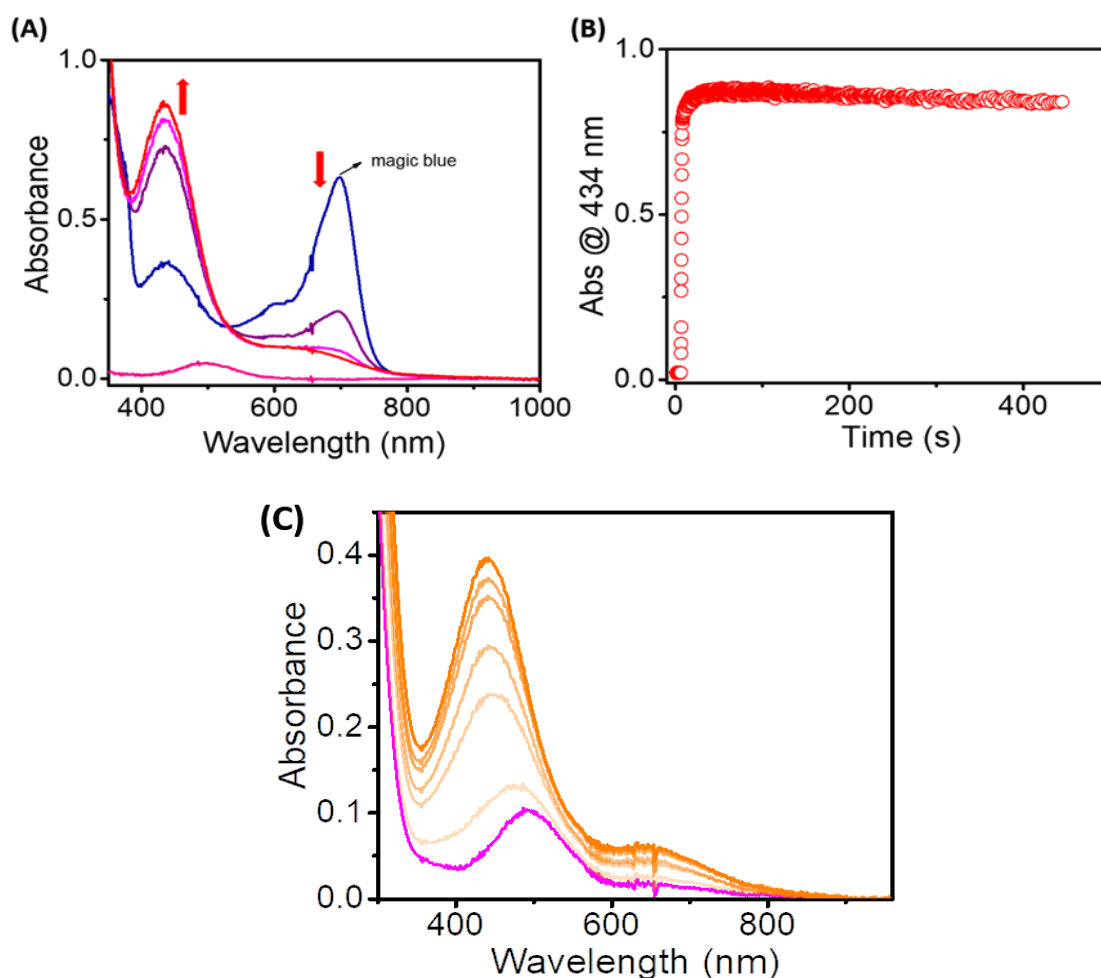
**Fig. S4.** (A) Scan rate (in mV/s) dependent cyclic voltammograms of **1** in MeOH:CH<sub>3</sub>CN (1:20) and (B) Differential pulse voltammograms (DPVs) of **1** in MeOH:CH<sub>3</sub>CN (1:20).



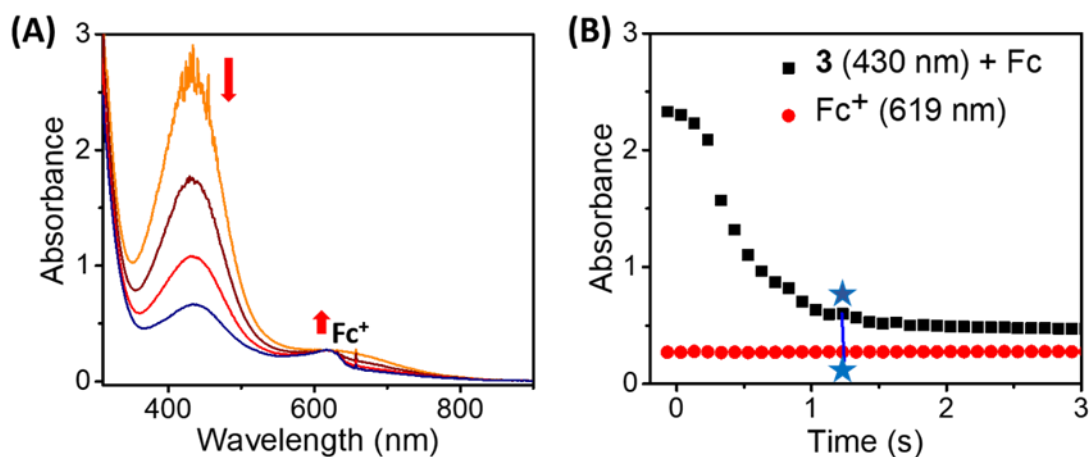
**Fig. S5.** (A) Time-dependent UV/Vis absorption spectral changes upon the reaction of **1** (1 mM in methanol) with 1 eq. *m*CPBA at -5 °C and (B) The corresponding changes in the absorption at 420 nm over time in seconds.



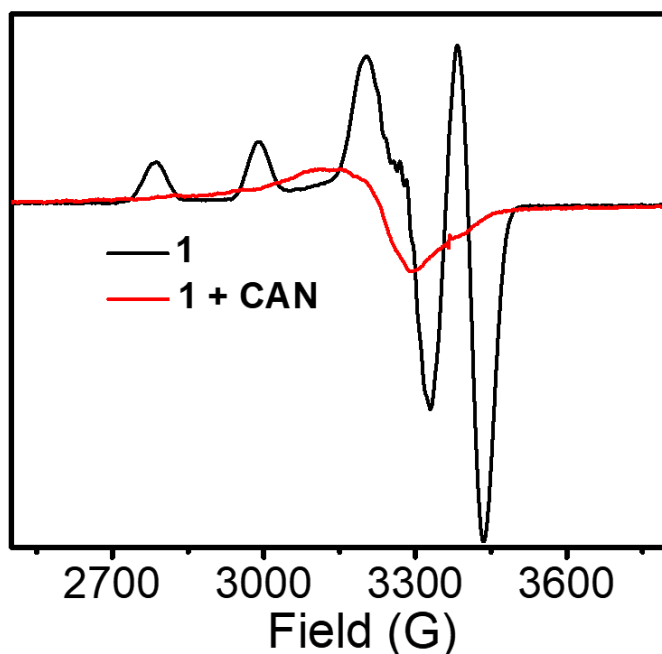
**Fig. S6.** (A) UV/Vis absorption spectral changes upon the reaction of **1** with 1 eq. CAN. Condition to generate **3**: 0.25 mM in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. CAN at -30 °C (B) The corresponding changes in the absorption of **3** at 434 nm over time at temperatures -30 °C, -5 °C and 25 °C. (C) Reaction of **3** (0.25 mM) with 2 eq. Fc at room temperature.



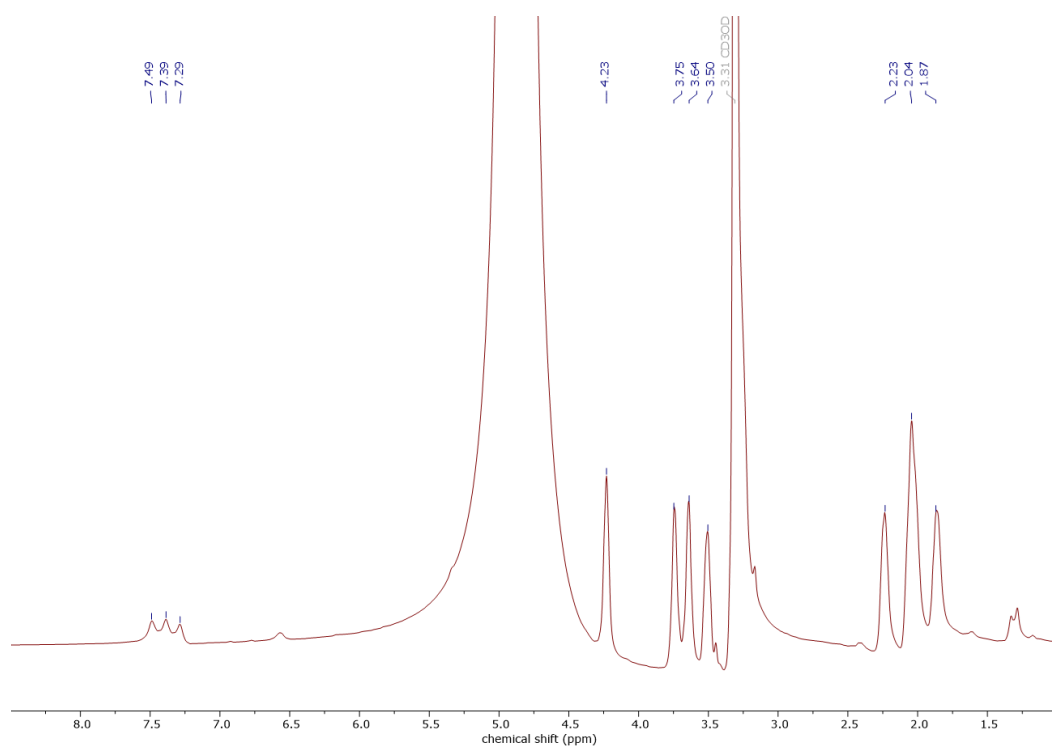
**Fig. S7.** (A) Time-dependent UV/Vis absorption spectral changes upon the reaction **1** with 1 eq. magic blue. Condition to generate **3**: 0.25 mM in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. magic blue at -30 °C. (B) The corresponding absorption changes at 434 nm. (C) Electrochemical oxidation of **3**. Conditions to generate **3**: 5 mM **1** in 100 mM TBAP dissolved in MeOH:CH<sub>3</sub>CN (1:20) and applied potential 0.6 V vs. Ag/AgCl.



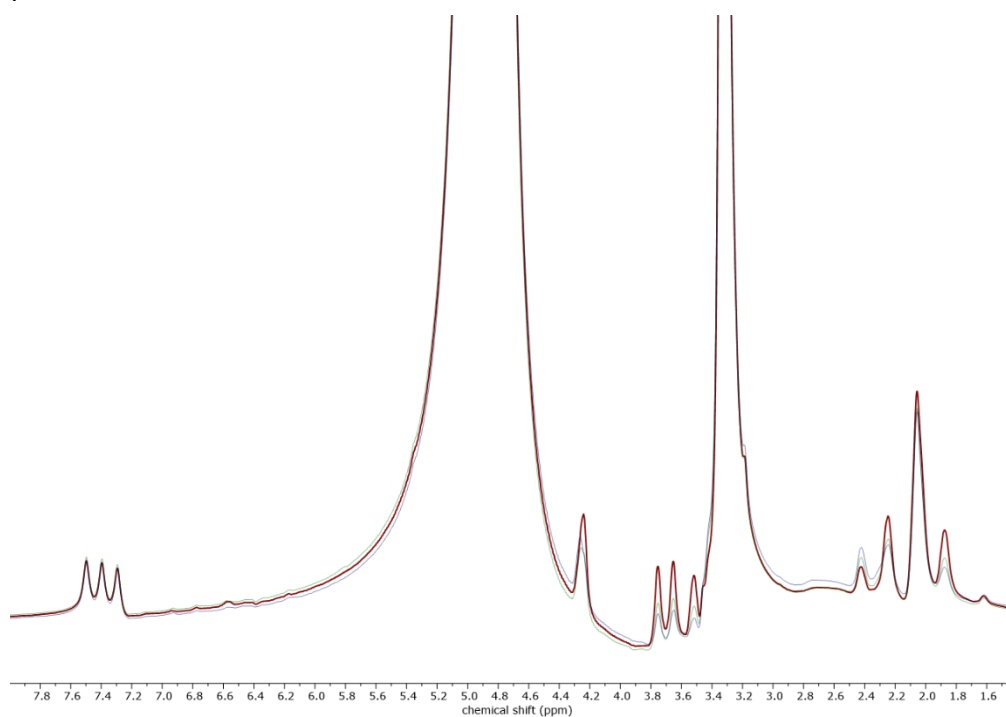
**Fig. S8.** (A) Time-dependent UV/Vis absorption spectral changes upon the reaction of **3** with 1 eq. Fc. *Condition to generate 3: 1 mM in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. mCPBA at -30 °C.* Note: The Fc added after the maximum accumulation of 430 nm band that takes approximately 400 s. (B) The corresponding absorption changes at 430 nm and 619 nm. \* The blue star marks the absorbance of ferrocenium, where all the 430 nm species have reacted with Fc to give Fc<sup>+</sup>.



**Fig. S9.** X-band EPR (Frequency = 9.432 GHz) spectrum of **1** and **3** measured at 120 K. Modulation amplitude 1.98 G; Modulation frequency 100 kHz, and Attenuation 18 dB. *Conditions to generate 3: 2 mM 1 in MeOH:CH<sub>3</sub>CN (1:20) + 1 eq. CAN at RT.*

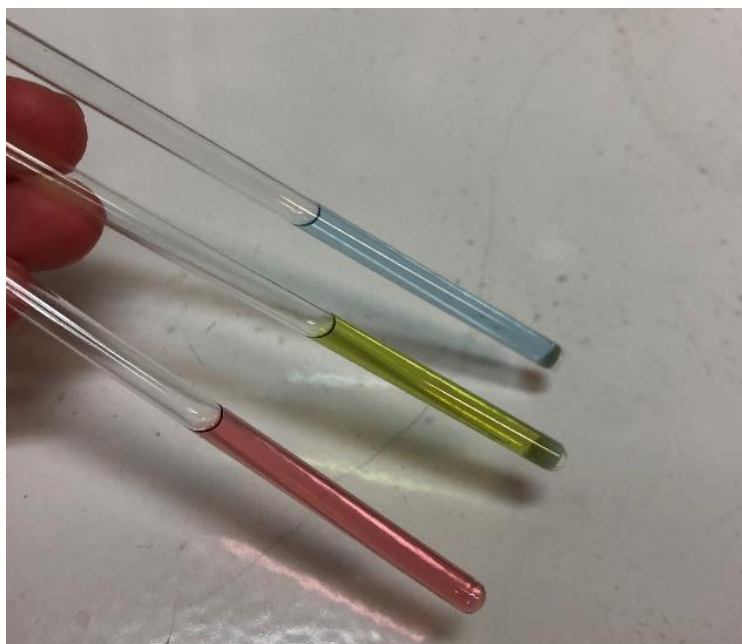


**Fig. S10.**  $^1\text{H}$ -NMR spectrum of **3**, generated by addition of 1 eq. CAN to 8 mM of **1** in  $\text{CD}_3\text{OD}$ . Species generated on ice and its spectrum taken at room temperature. The three peaks at ca. 7.4 ppm are due to  $\text{NH}_4^+$  from CAN.

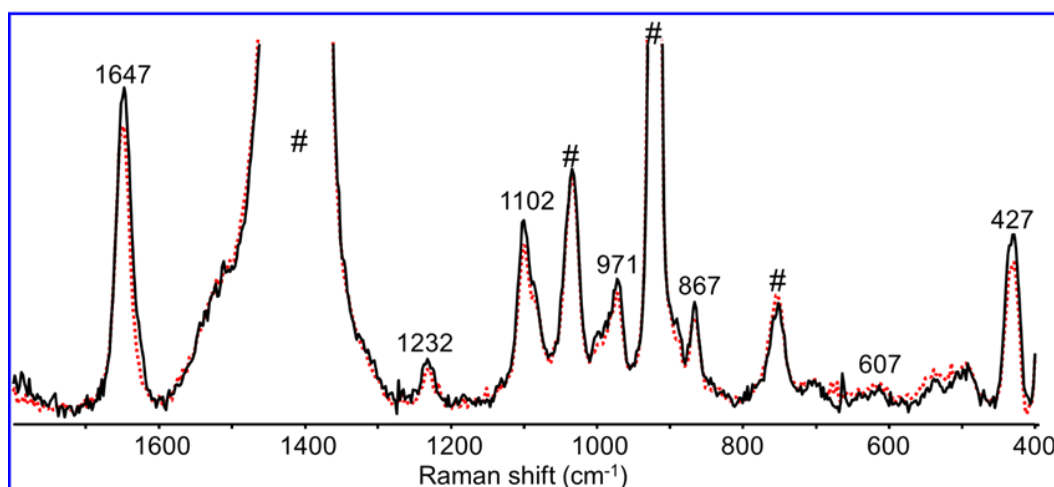


**Fig. S11.** Decay of **3** (generated from 8 mM **1** with 1 eq. CAN on ice) over time, 1 h (red), 2 h (green), 3 h (blue) after reaction. Spectra obtained at room temperature. The three peaks at ca. 7.4 ppm are due to  $\text{NH}_4^+$  from CAN.

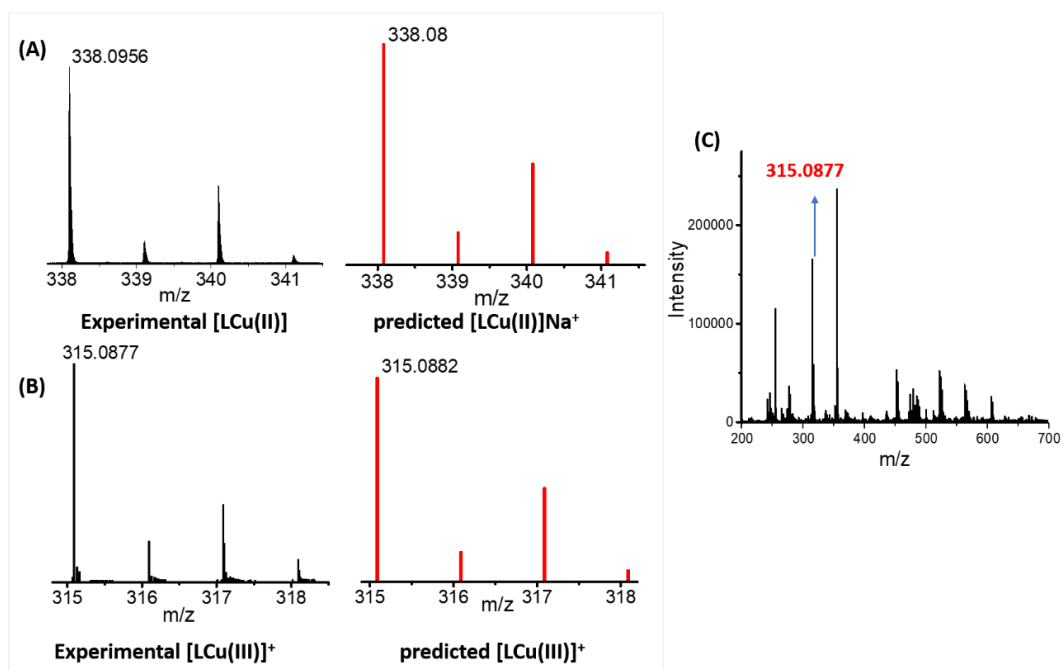




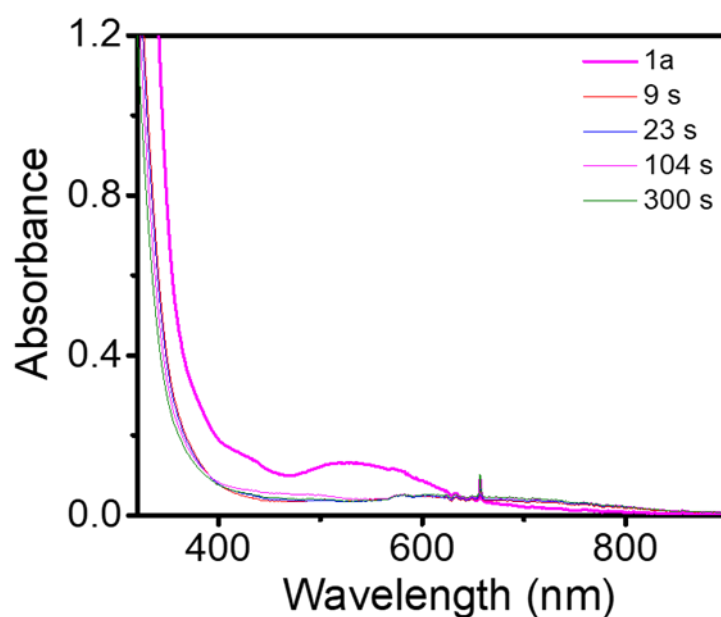
**Fig. S12.** NMR samples (8 mM in  $\text{CD}_3\text{OD}$ ) of **1** (pink, left), **3** (green, middle), and the decomposition product (blue, right).



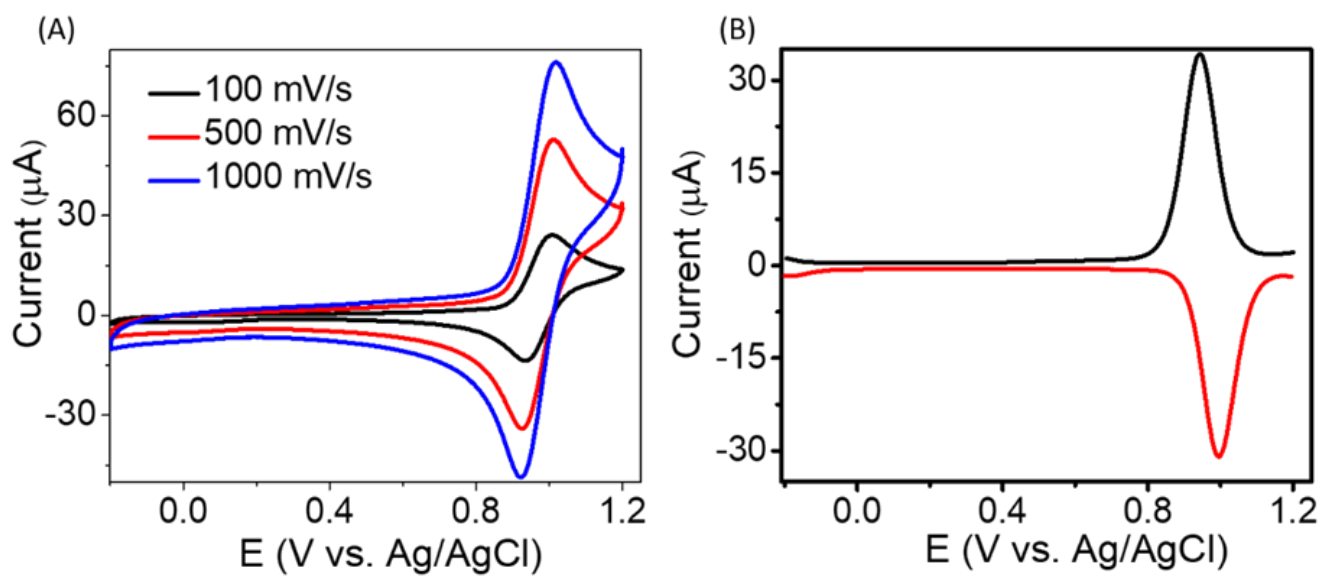
**Fig. S13.** Resonance Raman spectra ( $\lambda_{\text{ex}} = 473 \text{ nm}$ ) of 430 nm band. Condition to generate **3**: 1 mM in  $\text{MeOH}:\text{CH}_3\text{CN}$  (1:20) with 1 eq. CAN at  $-15^\circ\text{C}$  in the absence of  $\text{H}_2\text{O}^{18}$  (black solid line) and presence of  $\text{H}_2\text{O}^{18}$  (red dotted line).



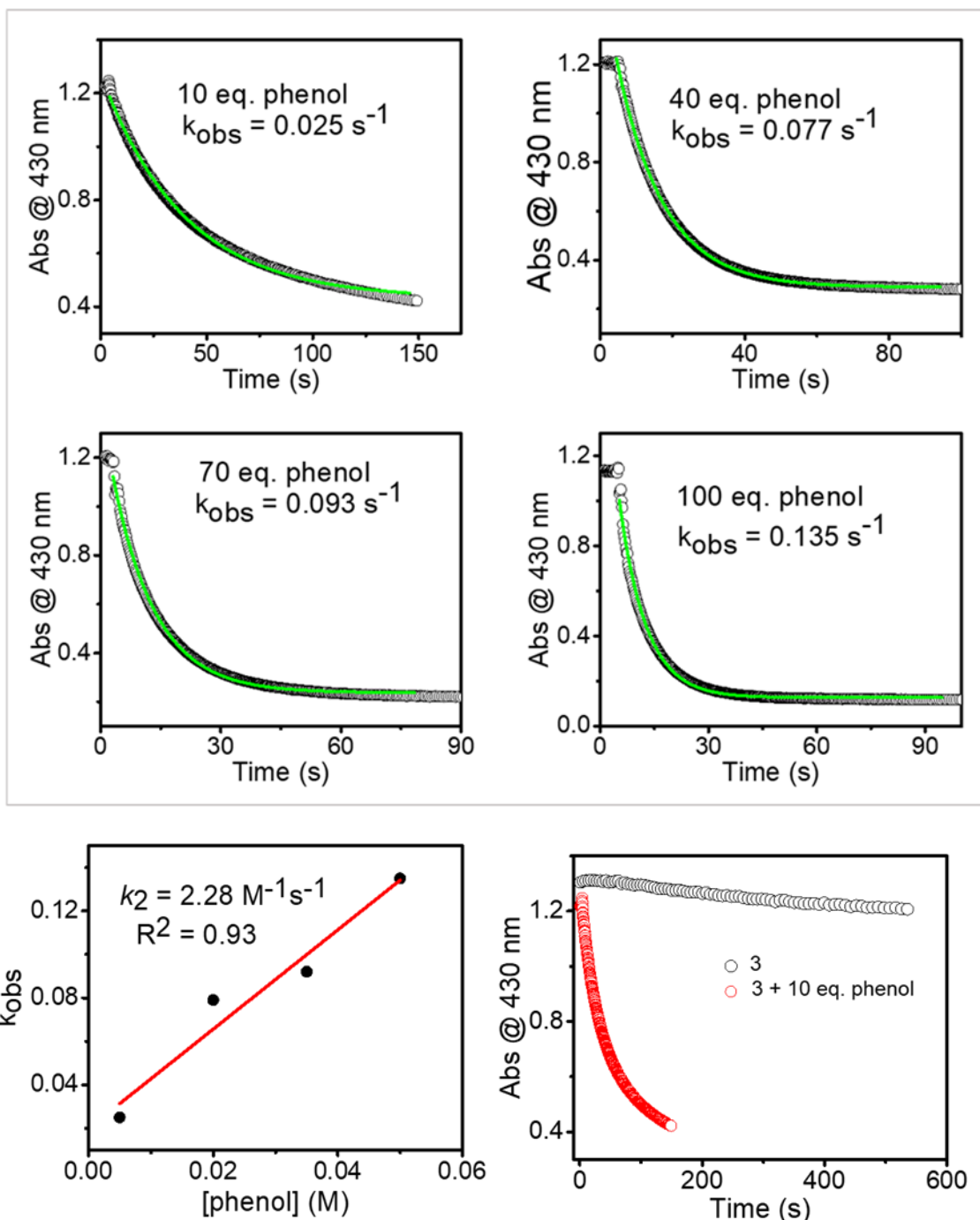
**Fig. S14.** (A) Experimental mass spectrum of [LCu(II)] in MeOH:CH<sub>3</sub>CN (1:20) and the predicted mass spectrum of [LCu(II)]Na<sup>+</sup>, (B) the experimental mass spectrum of the species generated upon addition of 1 eq. CAN to [LCu(II)] and the predicted spectra of [LCu(III)]<sup>+</sup>. Conditions to generate **3**: 2 mM of [LCu(II)] in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. CAN in at room temperature. (C) Full ESI-MS data of **3**.



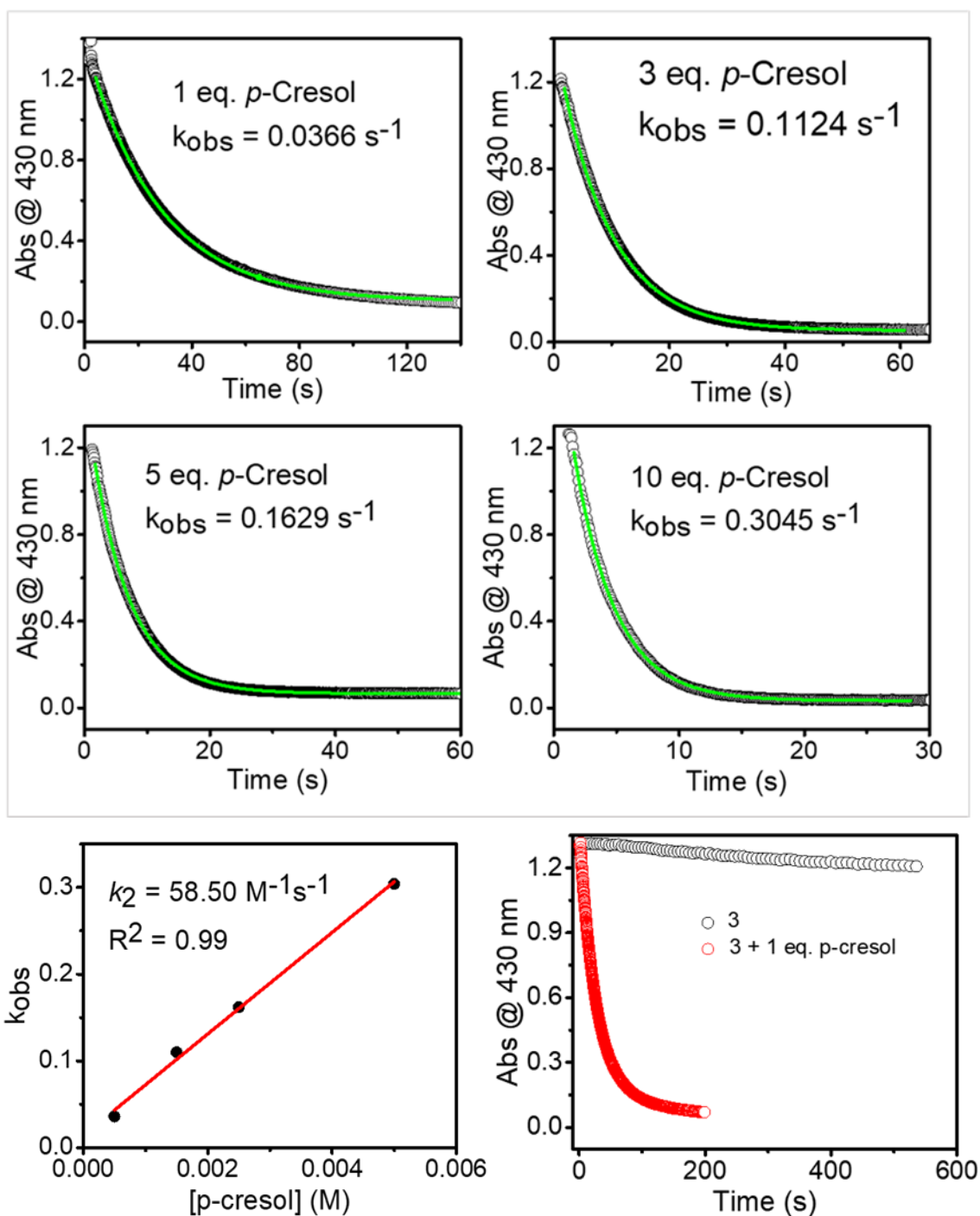
**Fig. S15.** Time-dependent UV/Vis absorption spectral changes upon the reaction of **1a** (1 mM in MeOH:CH<sub>3</sub>CN (1:20)) with 1 eq. *m*CPBA at -30 °C.



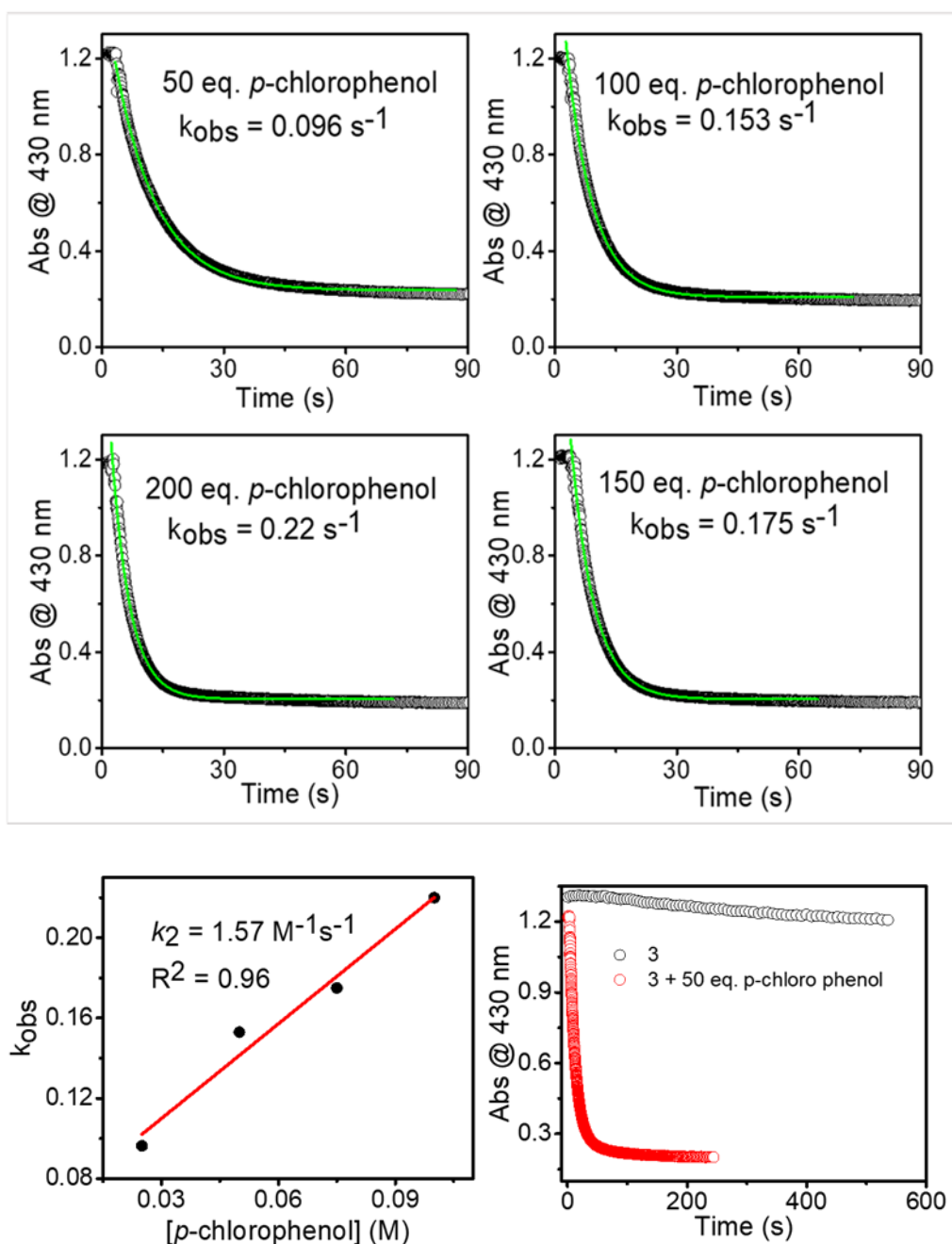
**Fig. S16.** (A) Scan rate (in mV/s) dependent cyclic voltammograms of **1a** in MeOH:CH<sub>3</sub>CN (1:20) and (B) DPVs of **1a** in MeOH : CH<sub>3</sub>CN (1:20).



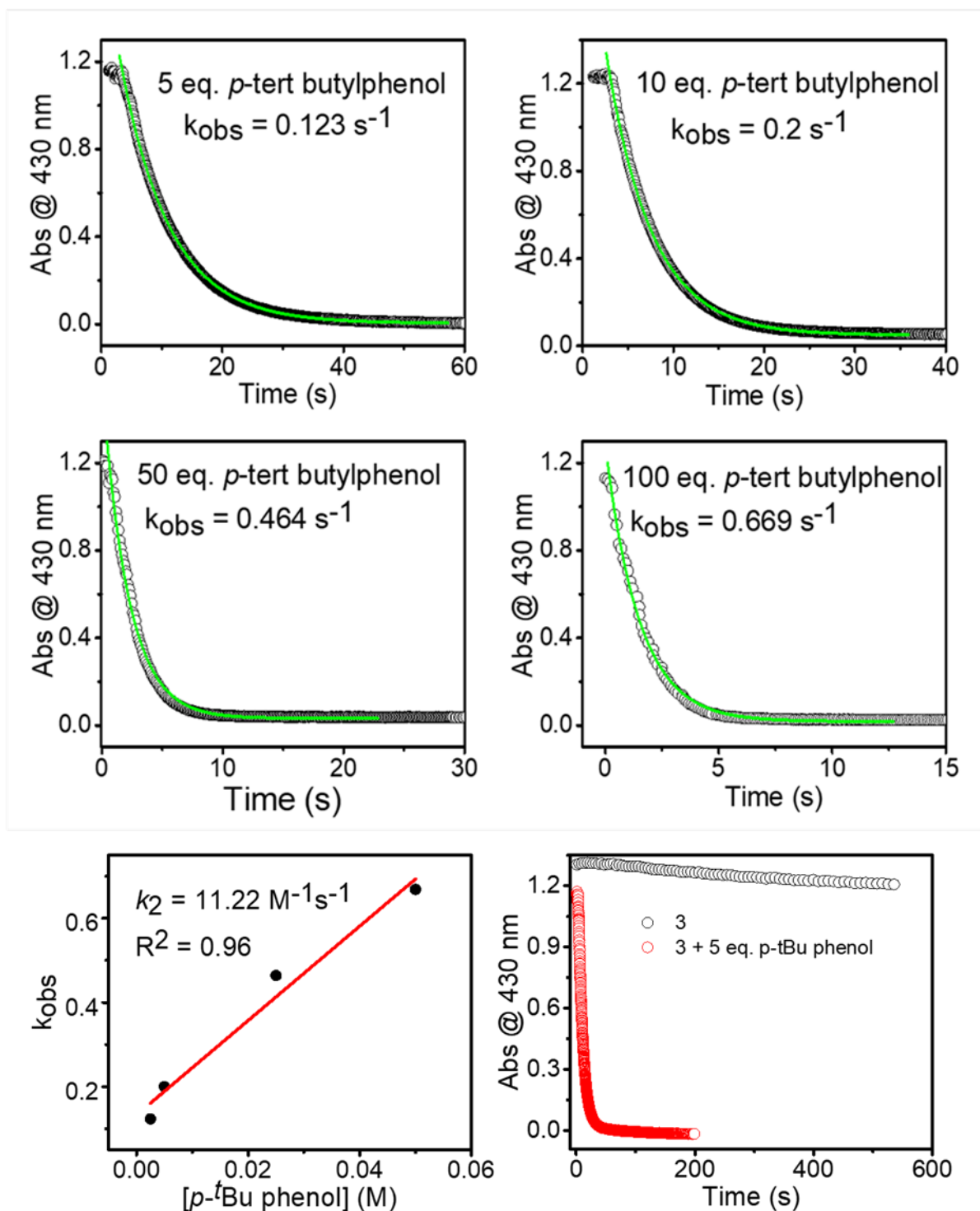
**Fig. S17.** Decay profile of **3** followed at 430 nm, with different equivalents of phenol and the corresponding  $k_{obs}$  values. Conditions to generate **3**: 0.5 mM in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. mCPBA at -30 °C. Note: The substrate added after the maximum accumulation of 430 nm band that takes approximately 500 s. (Bottom Left) A plot of  $k_{obs}$  vs [phenol] to obtain the second-order rate constant for the reaction of **3** with phenol. (Bottom right) Comparison of **3** natural decay and it's reactivity with 10 eq. phenol.



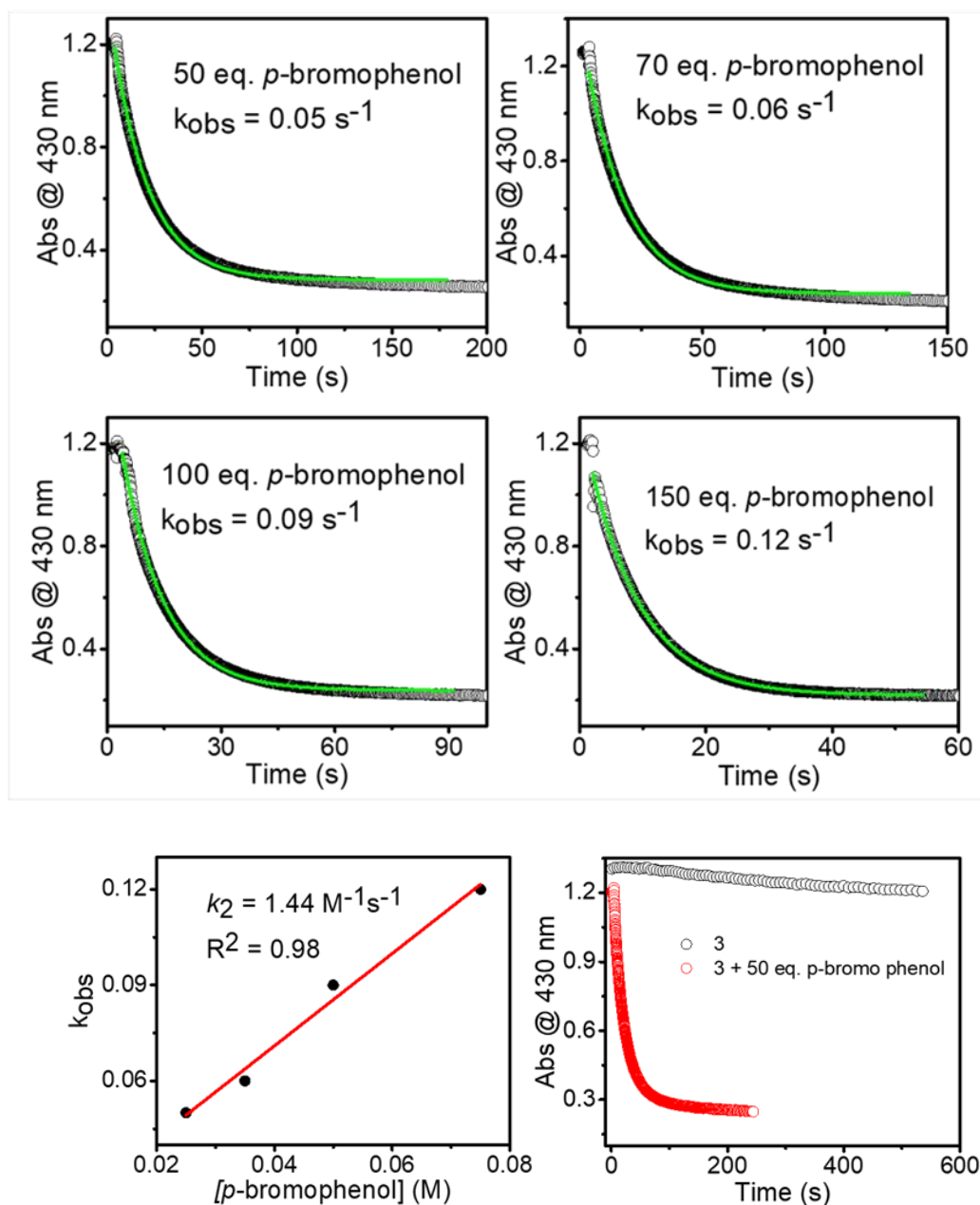
**Fig. S18.** Decay profile of **3** followed at 430 nm, with different equivalents of *p*-cresol and the corresponding  $k_{obs}$  values. *Conditions to generate 3*: 0.5 mM in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. *m*CPBA at -30 °C. Note: The substrate added after the maximum accumulation of 430 nm band that takes approximately 500 s. (Bottom left) A plot of  $k_{obs}$  vs [p-cresol] to obtain the second-order rate constant for the reaction of **3** with *p*-cresol. (Bottom right) Comparison of **3** natural decay and it's reactivity with 1 eq. *p*-cresol.



**Fig. S19.** Decay profile of **3** followed at 430 nm, with different equivalents of *p*-chlorophenol and the corresponding  $k_{obs}$  values. Conditions to generate **3**: 0.5 mM in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. *m*CPBA at -30 °C. Note: The substrate added after the maximum accumulation of 430 nm band that takes approximately 500 s. (Bottom left) A plot of  $k_{obs}$  vs [p-chlorophenol] to obtain the second-order rate constant for the reaction of **3** with *p*-chlorophenol. (Bottom right) Comparison of **3** natural decay and it's reactivity with 50 eq. *p*-chloro phenol.

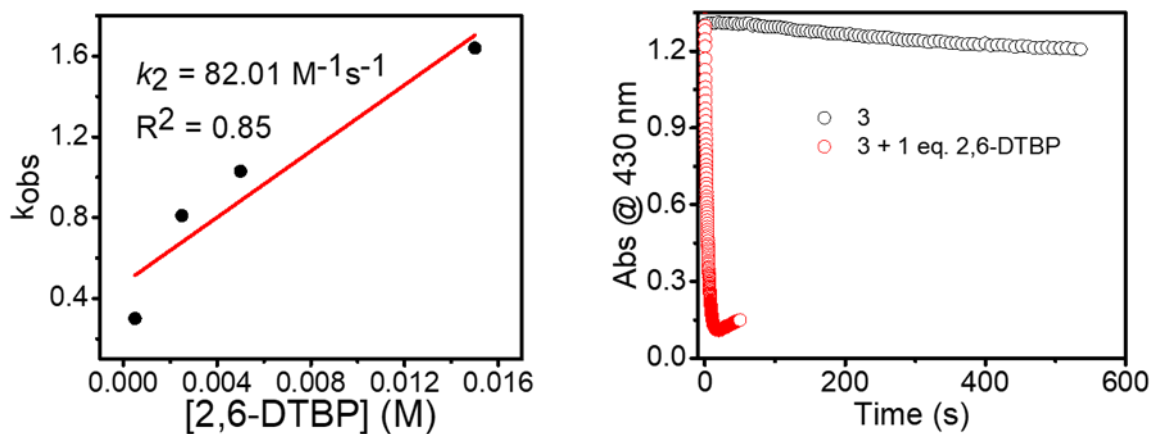
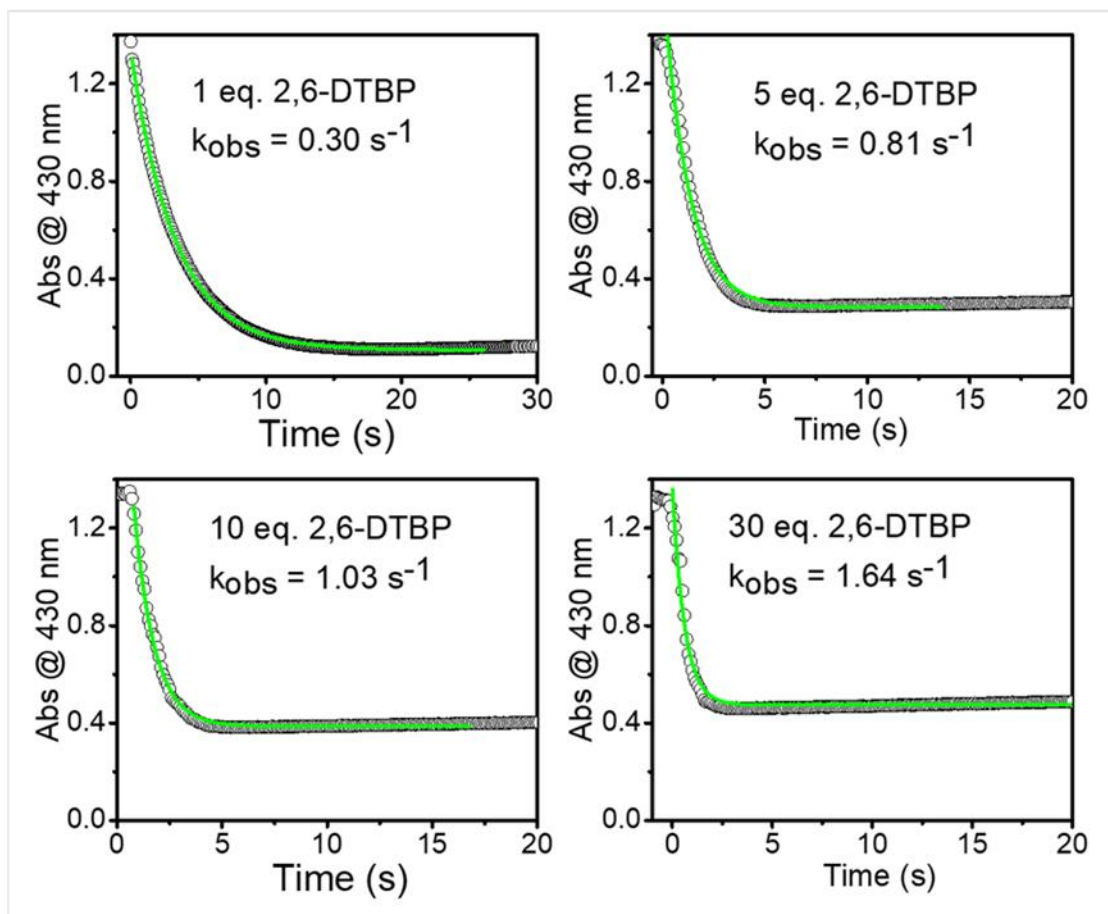


**Fig. S20.** Decay profile of **3** followed at 430 nm, with different equivalents of *p*-tert-butylphenol and the corresponding  $k_{obs}$  values. Conditions to generate **3**: 0.5 mM in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. mCPBA at -30 °C. Note: The substrate added after the maximum accumulation of 430 nm band that takes approximately 500 s. (Bottom left) A plot of  $k_{obs}$  vs [*p*-tert-butylphenol] to obtain the second-order rate constant for the reaction of **3** with *p*-tert-butylphenol. (Bottom right) Comparison of **3** natural decay and it's reactivity with 5 eq. *p*-tBu phenol.

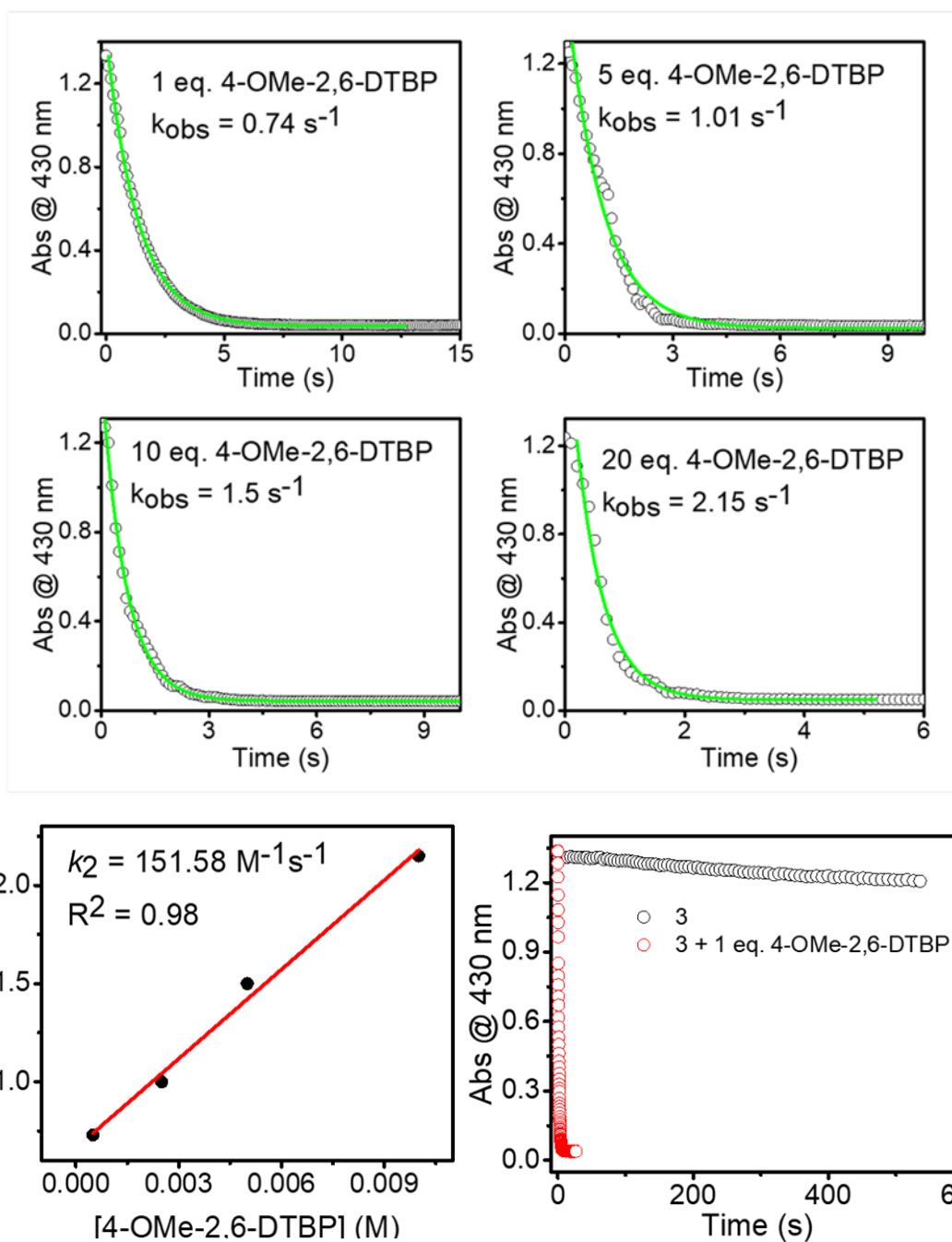


**Fig. S21.** Decay profile of **3** followed at 430 nm, with different equivalents of *p*-bromophenol and the corresponding  $k_{obs}$  values. *Conditions to generate 3*: 0.5 mM in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. *m*CPBA at -30 °C. Note: The substrate added after the maximum accumulation of 430 nm band that takes approximately 500 s. (Bottom left) A plot of  $k_{obs}$  vs  $[p\text{-bromophenol}]$  to obtain the second-order rate constant for the reaction of **3** with *p*-bromophenol. (Bottom right) Comparison of **3** natural decay and it's reactivity with 50 eq. *p*-bromo phenol.

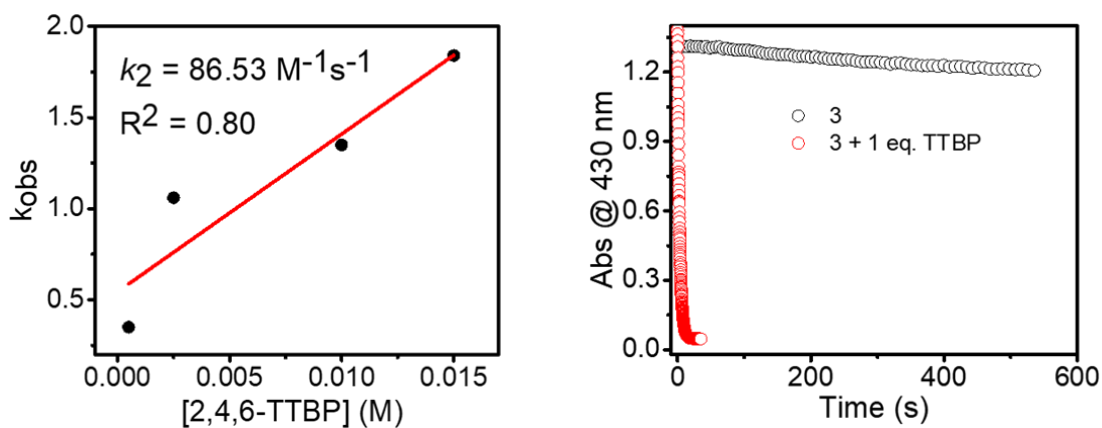
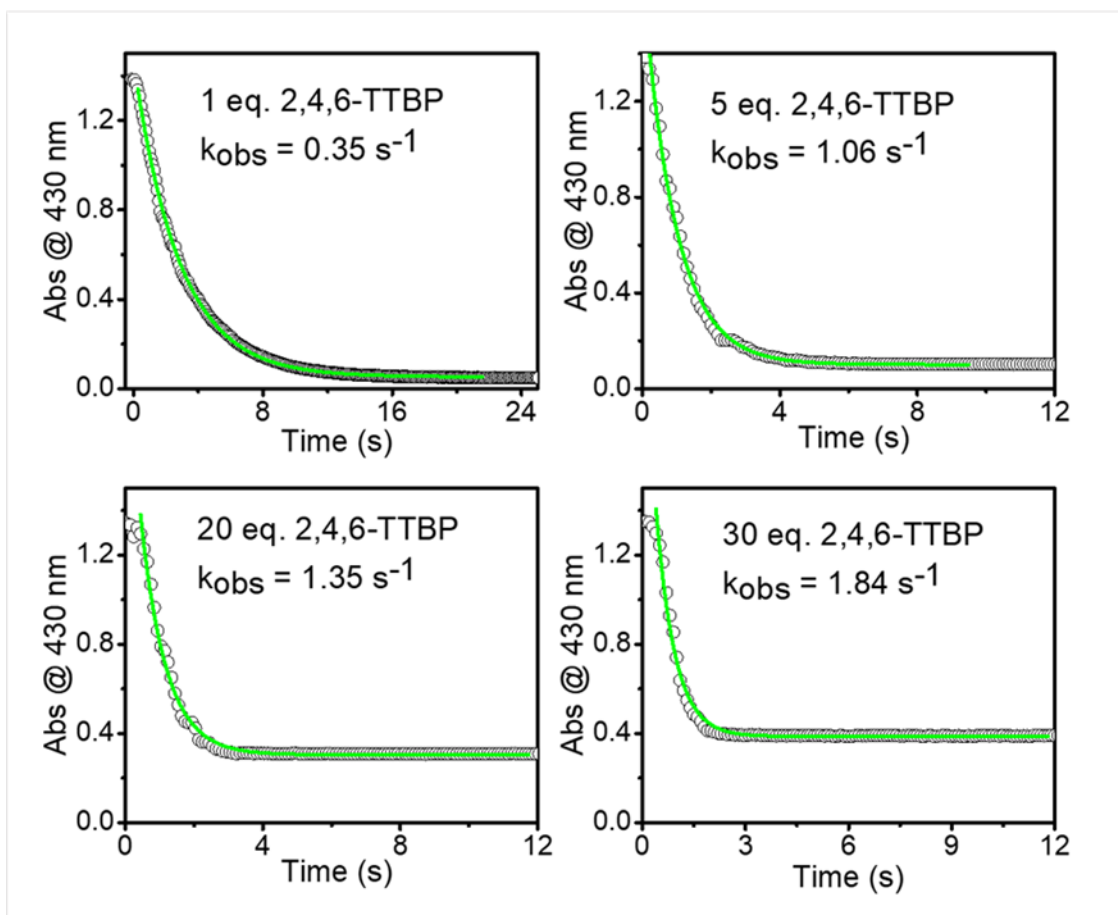




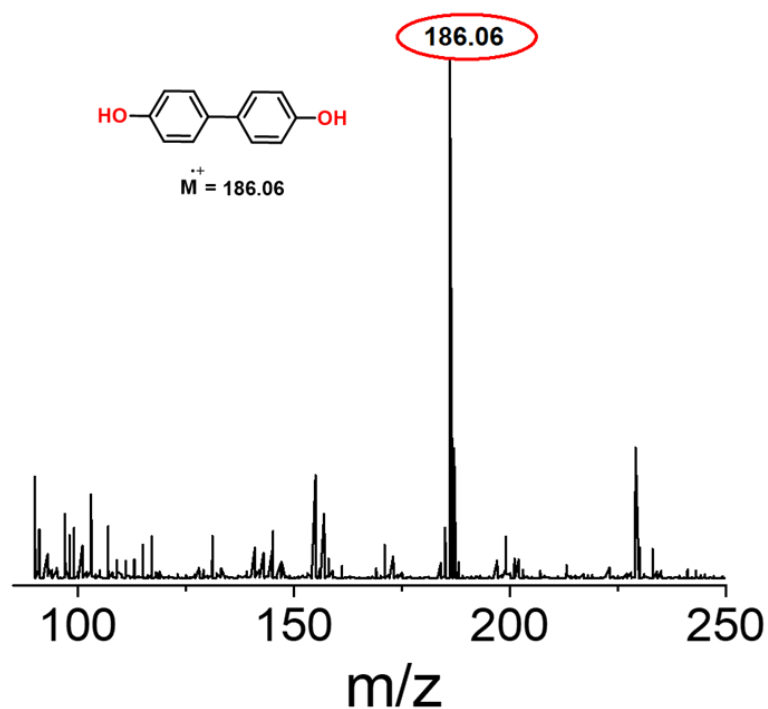
**Fig. S22.** Decay profile of **3** followed at 430 nm, with different equivalents of 2,6-DTBP and the corresponding  $k_{obs}$  values. *Conditions to generate 3: 0.5 mM in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. mCPBA at -30 °C.* Note: The substrate added after the maximum accumulation of 430 nm band that takes approximately 500 s. (Bottom left) A Plot of  $k_{obs}$  vs [2,6-DTBP] to obtain the second-order rate constant for the reaction of **3** with 2,6-DTBP. (Bottom right) Comparison of **3** natural decay and it's reactivity with 1 eq. 2,6-DTBP.



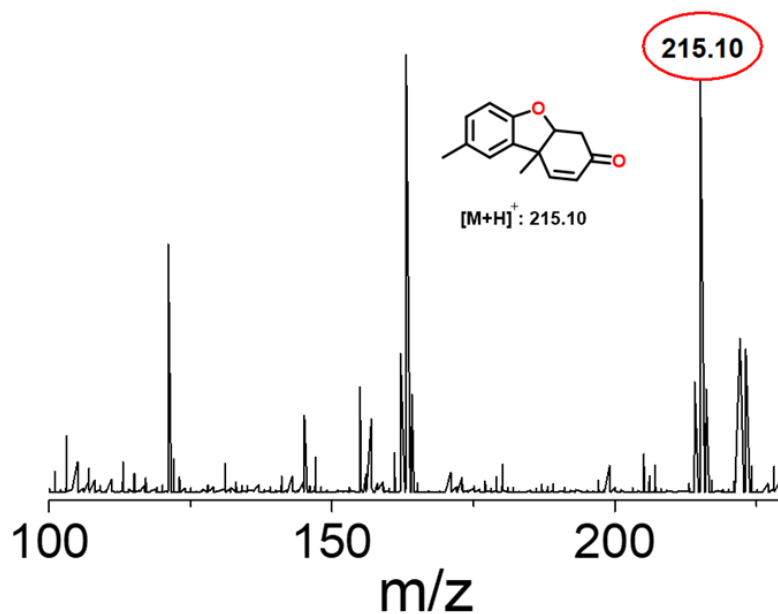
**Fig. S23.** Decay profile of **3** followed at 430 nm, with different equivalents of 4-OMe-2,6-DTBP and the corresponding  $k_{obs}$  values. Conditions to generate **3**: 0.5 mM in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. mCPBA at -30 °C. Note: The substrate added after the maximum accumulation of 430 nm band that takes approximately 500 s. (bottom left) A plot of  $k_{obs}$  vs [4-OMe-2,6-DTBP] to obtain the second-order rate constant for the reaction of **3** with 4-OMe-2,6-DTBP. (Bottom right) Comparison of **3** natural decay and it's reactivity with 1 eq. 4-OMe-2,6-DTBP.



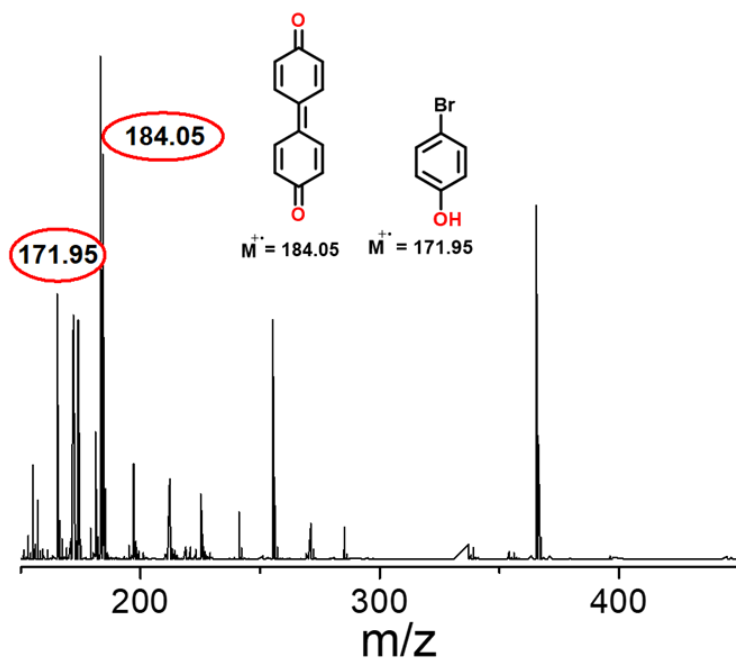
**Fig. S24.** Decay profile of **3** followed at 430 nm, with different equivalents of 2,4,6-TTBP and the corresponding  $k_{obs}$  values. *Conditions to generate 3: 0.5 mM in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. mCPBA at -30 °C.* Note: The substrate added after the maximum accumulation of 430 nm band that takes approximately 500 s. (Bottom left) A plot of  $k_{obs}$  vs [2,4,6-TTBP] to obtain the second-order rate constant for the reaction of **3** with 2,4,6-TTBP. (Bottom right) Comparison of **3** natural decay and it's reactivity with 1 eq. TTBP.



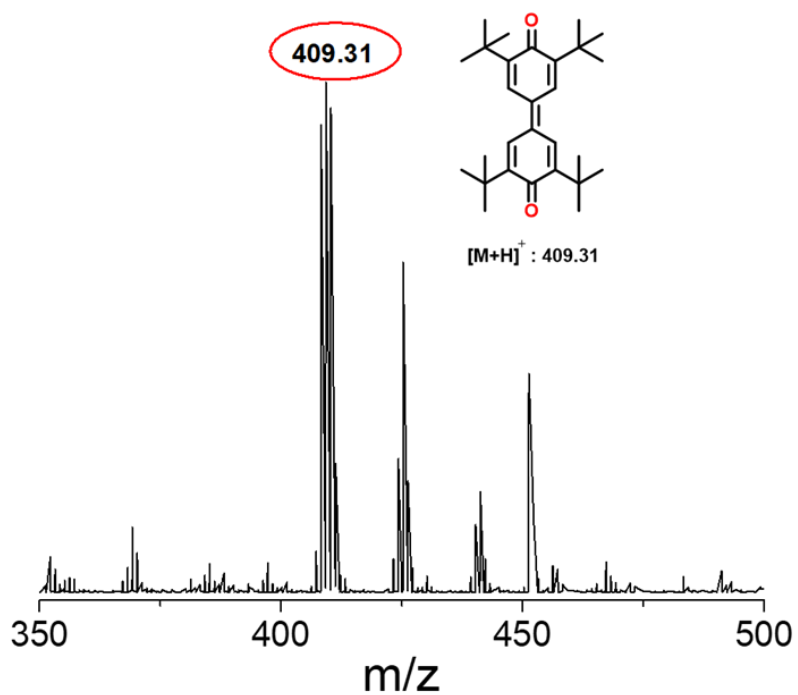
**Fig. S25.** Product analysis of the reaction of **3** with 20 eq. phenol by APCI-MS. Conditions to generate **3**: 2.0 mM **1** in MeOH:CH<sub>3</sub>CN (1:20) + 1 eq. *m*CPBA.



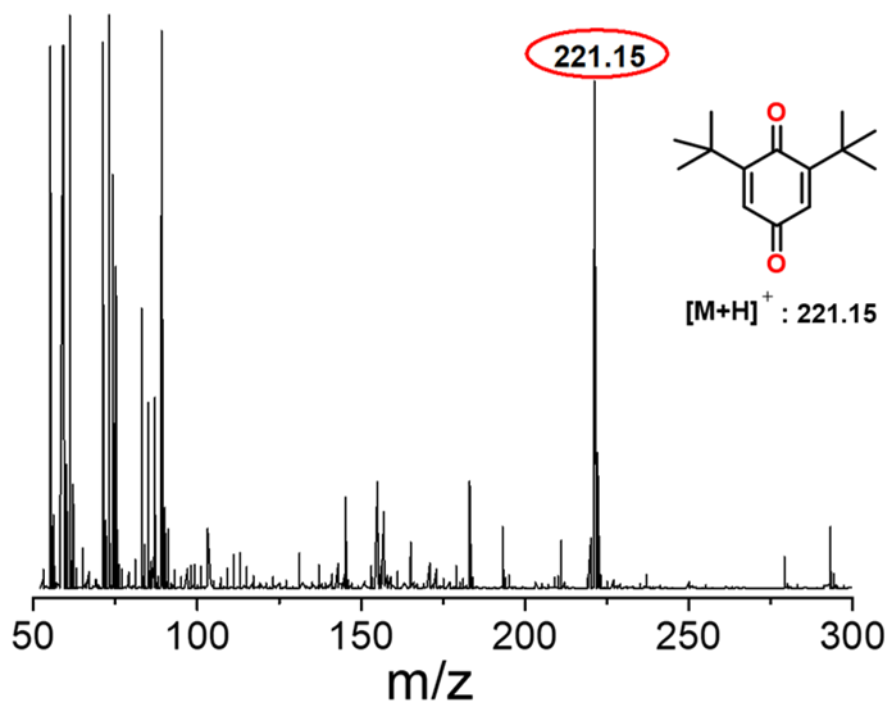
**Fig. S26.** Product analysis of the reaction of **3** with 20 eq. *p*-cresol by APCI-MS. Conditions to generate **3**: 2.0 mM **1** in MeOH:CH<sub>3</sub>CN (1:20) + 1 eq. *m*CPBA.



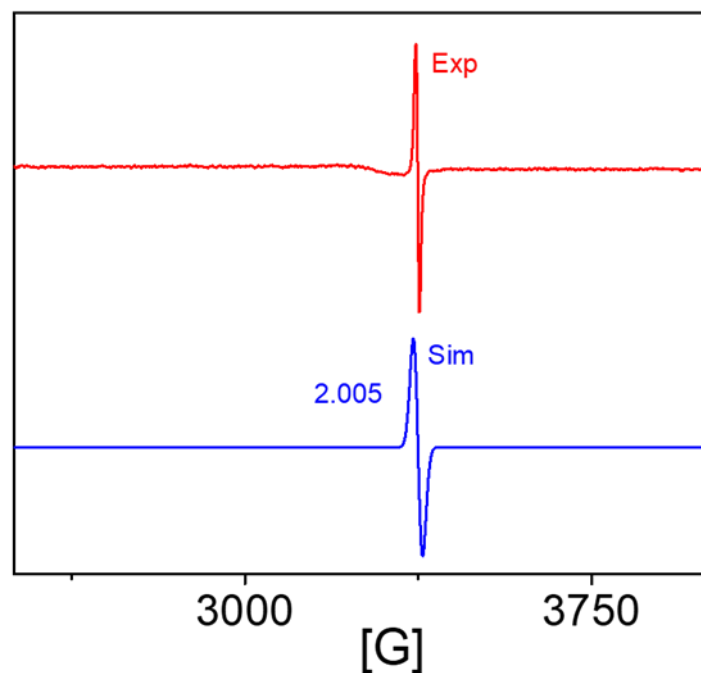
**Fig. S27.** Product analysis of the reaction of **3** with 20 eq. p-bromophenol by APCI-MS. Conditions to generate **3**: 2.0 mM **1** in MeOH:CH<sub>3</sub>CN (1:20) + 1 eq. *m*CPBA.



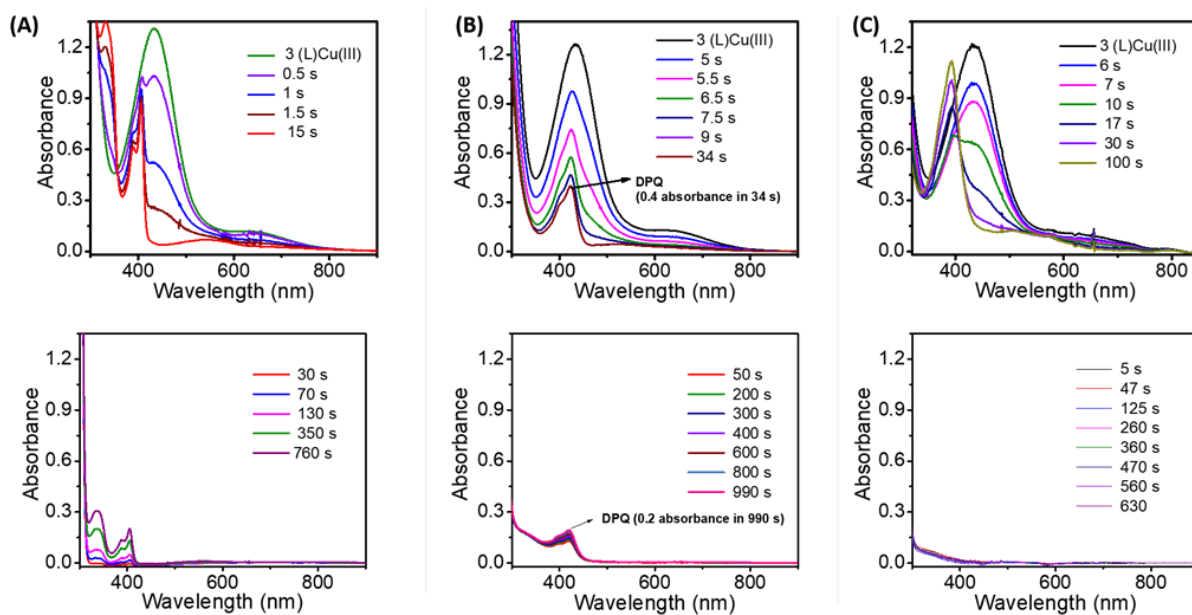
**Fig. S28.** Product analysis of the reaction of **3** with 20 eq. 2,6-DTBP by APCI-MS. Conditions to generate **3**: 2.0 mM **1** in MeOH:CH<sub>3</sub>CN (1:20) + 1 eq. *m*CPBA.



**Fig. S29.** Product analysis of the reaction of **3** with 20 eq. 4-OMe-2,6-DTBP by APCI-MS. Conditions to generate **3**: 2.0 mM **1** in MeOH:CH<sub>3</sub>CN (1:20) + 1 eq. *m*CPBA.



**Fig. S30.** X-band EPR (Frequency = 9.469 GHz) spectrum of TTBP<sup>•</sup> formed upon the reaction of **3** with 2,4,6-TTBP in MeOH:CH<sub>3</sub>CN (1:20) measured at 120 K; Modulation amplitude 1.98 G; Modulation frequency 100 kHz, and Attenuation 18 dB. (Red) experimental and (blue) simulated. Simulated parameters :  $g_x = g_y = g_z = 2.005$ .



**Fig. S31.** (A) Reaction of **3** with 30 eq. 4-OMe-2,6-DTBP at -30 °C (Top) and the blank reaction of 1 eq. *m*CPBA with 30 eq. 4-OMe-2,6-DTBP at RT (Bottom). (B) Reaction of **3** with 30 eq. 2,6-DTBP at -30 °C (Top) and the blank reaction of 1 eq. *m*CPBA with 30 eq. 2,6-DTBP at RT (Bottom). (C) Reaction of **3** with 100 eq. phenol at -30 °C (Top) and the blank reaction of 1 eq. *m*CPBA with 100 eq. phenol at RT (Bottom). *Conditions to generate 3*: 0.5 mM in MeOH:CH<sub>3</sub>CN (1:20) with 1 eq. *m*CPBA at -30 °C.