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Electronic Supplementary Information

Aromatic Hydroxylation of Anthracene Derivatives by a Chromium(III)-Superoxo Complex *via* Proton-Coupled Electron Transfer

Tarali Devi,[a] Yong-Min Lee,[a] Wonwoo Nam,*[a] and Shunichi Fukuzumi*[a,b]

[a]Department of Chemistry and Nano Science, Ewha Womans University, Seoul 03760,
Korea
[b]Faculty of Science and Engineering, Meijo University, Nagoya, Aichi 468-8502, Japan

* To whom correspondence should be addressed.
E-mail: wwnam@ewha.ac.kr, fukuzumi@chem.eng.osaka-u.ac.jp

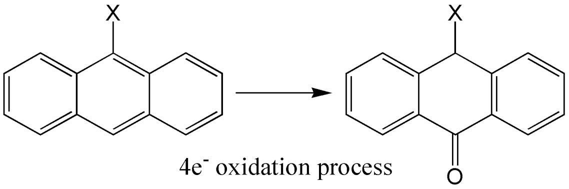
Experimental Section

Materials. All chemicals, which were of reagent-grade quality, were obtained commercially and used without further purification, unless otherwise noted. Solvents were dried according to published procedures and distilled under an Ar atmosphere prior to use.[S1] Anthracene and its derivatives, such as 9-methylanthracne, 9-bromoanthracene, 9-anthracenecarboxaldehyde and 9,10-dimethylanthracene, were purchased from Aldrich Chemical Co. and used as received. Triflurомethanesulfonic acid (triflic acid; CF_3SO_3H; HOTf) was purchased from Tokyo Chemical Industry Co., LTD. The deuterated anthracene compound (anthracene-d^{10}) was also purchased from Aldrich Chemical Co. and used as received. $^{18}O_2$ gas (98% ^{18}O-enriched) was purchased from ICON Services Inc. (Summit, NJ. USA). The chromium complexes, $[(TMC)Cr^{II}(Cl)]Cl$, $[(TMC)Cr^{III}(O_2^{\bullet-})(Cl)]Cl$ (**1**), and $[(TMC)Cr^{III}(^{18}O_2^{\bullet-})(Cl)]Cl$ (**1**-^{18}O), were synthesized according to the literature methods.[S2, S3]

Instrumentation. UV-vis spectra were recorded on a Hewlett Packard 8453 diode array spectrophotometer equipped with a UNISOKU Scientific Instruments Cryostat USP-203A for low-temperature experiments or on a UNISOKU RSP-601 stopped-flow spectrometer equipped with a MOS-type highly sensitive photodiode-array. Cold spray ionization mass (CSI-MS) spectra were collected on a JMS-T100CS (JEOL) mass spectrometer equipped with a CSI source [conditions: needle voltage = 2.2 kV, orifice 1 current = 50 – 500 nA, orifice 1 voltage = 0 – 20 V, ringlens voltage = 10 V, ion source temperature = 5 °C, spray temperature = –40 °C]. X-band CW-EPR spectra were recorded at 5 K using an X-band Bruker EMX-plus spectrometer equipped with a dual mode cavity (ER 4116DM) [experimental parameters: microwave frequency = 9.647 GHz, microwave power = 1.0 mW, modulation amplitude = 10 G, gain = 1×10^4, modulation frequency = 100 kHz, time constant = 40.96 ms, conversion time = 81.00 ms]. Product analysis was performed by ^{1}H NMR measurements on a Bruker model digital AVANCE III 400 FT-NMR spectrometer. Product analysis was also performed with Thermo Finnigan (Austin, Texas, USA) FOCUS DSQ (dual stage quadrupole) mass spectrometer interfaced with Finnigan FOCUS gas chromatograph (GC-MS).

Kinetic Measurements. Typically, kinetic measurements for the oxidation of anthracene and its derivatives, such as 9-substituted anthracene derivatives (XAn: 9-methylanthracene, 9-bromoanthracene and 9-anthracenecarboxaldehyde) and 9,10-dimethylanthracene, by $[(TMC)Cr^{III}(O_2^{\bullet-})]^{2+}$ (**1**) in the presence of HOTf (2.5 mM) were performed on a UNISOKU RSP-601 stopped-flow spectrometer in MeCN at 233 K under the conditions such that [**1**] = [substrate]. Rates of oxidation of anthracene and 9-substituted anthracene derivatives (XAn) by **1** were monitored by following the decay of the absorption band at 550 nm due to **1** in the presence of HOTf (2.5 mM) in MeCN at 233 K. The second-order rate constants (k_{ox}) for 6-electron oxidation of anthracene, 4-electron oxidation of XAn, and 2-electron oxidation of 9,10-dimethylanthracene by **1** (3-electron oxidant) in the presence of HOTf (2.5 mM) in MeCN at 233 K were determined using eqn (5) in text, eqn (S5) and eqn (S10) in ESI, respectively.

Determination of k_{ox} value for the four-electron oxidation of substrate by 3-electron oxidant.



rate = $-d[Cr^{III}(O_2)]/dt = k_{ox}[Cr^{III}(O_2)][XAn]$ (S1)

$[Cr^{III}(O_2)]_0 = [Cr^{III}(O_2)] + [Cr^{III}]$ (S2)

$[XAn]_0 = [XAn] + (4/3)[Cr^{III}]$ (S3)

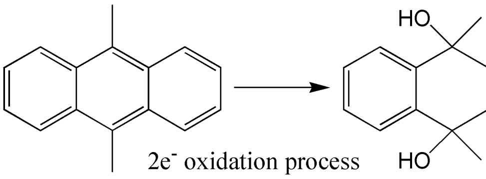
Thus, $-d[Cr^{III}(O_2)]/dt = k_{ox}[Cr^{III}(O_2)]([XAn]_0 - (4/3)[Cr^{III}(O_2)]_0 + (4/3)[Cr^{III}(O_2)])$ (S4)

Solving the differential eqn (S4) with eqns. (S2) and (S3) gives eqn (S5),

$\log [x/(C + (4/3)x)] = -(C/2.3)k_{ox}t + \log [x_0/(C + (4/3)x_0)]$ (S5)

where $x = [Cr^{III}(O_2)]$, $x_0 = [Cr^{III}(O_2)]_0$, $C = [XAn]_0 - (4/3)[Cr^{III}(O_2)]_0$, $x_0/(C + (4/3)x_0) = 1$. Thus, plot of $\log[x/(C + (4/3)x)]$ *vs.* t gives a straight line that passes through zero with slope = $-(C/2.3)k_{ox}$, where C is $-(1/3)x_0$.

Determination of k_{ox} value for the two-electron oxidation of substrate by 3-electron oxidant.



rate = $-d[Cr^{III}(O_2)]/dt = k_{ox}[Cr^{III}(O_2)][Me_2An]$ (S6)

$[Cr^{III}(O_2)]_0 = [Cr^{III}(O_2)] + [Cr^{III}]$ (S7)

$[Me_2An]_0 = [Me_2An] + (2/3)[Cr^{III}]$ (S8)

Thus, $-d[Cr^{III}(O_2)]/dt = k_{ox}[Cr^{III}(O_2)]([Me_2An]_0 - (2/3)[Cr^{III}(O_2)]_0 + (2/3)[Cr^{III}(O_2)])$ (S9)

Solving the differential eqn (S9) with eqns (S7) and (S8) gives eqn (S10),

$\log[x/(C + (2/3)x)] = -(C/2.3)k_{ox}t + \log[x_0/(C + (2/3)x_0)]$ (S10)

where $x = [Cr^{III}(O_2)]$, $x_0 = [Cr^{III}(O_2)]_0$, $C = [Me_2An]_0 - (2/3)[Cr^{III}(O_2)]_0$, $x_0/(C + (2/3)x_0) = 1$. Thus, plot of $\log[x/(C + (2/3)x)]$ *vs.* t gives a straight line that passes through zero with slope = $-(C/2.3)k_{ox}$, where C is $(1/3)x_0$.

References

S1 W. L. F. Armarego, C. L. L. Chai, in *Purification of Laboratory Chemicals*, 6th ed., Pergamon Press, Oxford, 2009.

S2 J. Cho, J. Woo and W. Nam, *J. Am. Chem. Soc.*, 2010, **132**, 5958.

S3 J. Cho, J. Woo and W. Nam, *J. Am. Chem. Soc.*, 2012, **134**, 11112.

Table S1 Second-order rate constants (k_{ox}) determined in the oxidation of anthracene by **1** in the presence of various concentrations of HOTf in MeCN at 233 K.

[HOTf], mM	k_{ox}, M^{-1} s^{-1}
2.5	4.1(4) × 10
5.0	$1.0(1) \times 10^2$
7.5	$2.3(2) \times 10^2$
10.0	$4.6(3) \times 10^2$

Table S2 Second-order rate constants (k_{ox}) determined in the oxidation of anthracene and its derivatives by **1** in the presence of HOTf (2.50 mM) in MeCN at 233 K

Substrate	E_{ox}, V *vs*. SCE	k_{ox}, M^{-1} s^{-1}
9,10-dimethylanthracene	1.05[a]	$4.8(4) \times 10^2$
9-methylanthracene	1.11[a]	$1.3(1) \times 10^2$
anthracene	1.19[a]	$4.1(4) \times 10$
9-bromoanthracene	1.30[a]	$3.3(3) \times 10$
9-anthracenecarboxaldehyde	1.37[b]	5.0(4)

[a] Taken from the reference: S. Fukuzumi, K. Okhubo and T. Okamoto, *J. Am. Chem. Soc.*, 2002, **124**, 14147. [b] Taken from the reference: S. Okazaki, M. Oyama and S. Nomura, *Electroanalysis*, 1997, **9**, 1242.

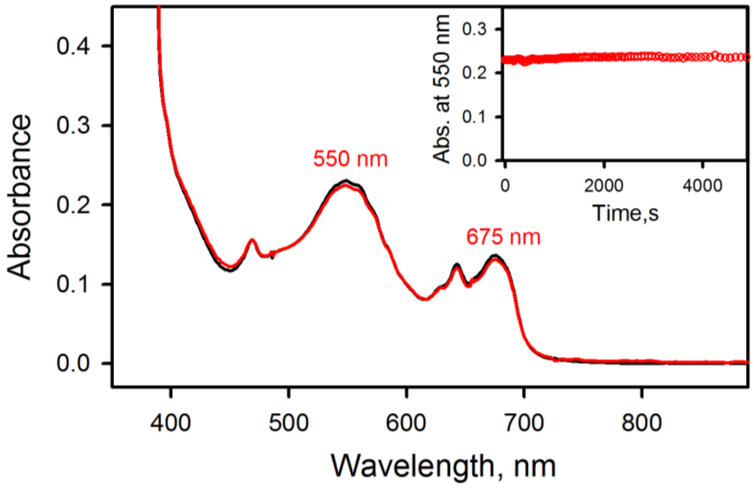


Fig. S1 UV-vis spectra of **1** (1.0 mM) in the absence (red line) and presence (black line) of anthracene (1.0 mM) in MeCN at 233 K. No reaction between **1** and anthracene was observed.

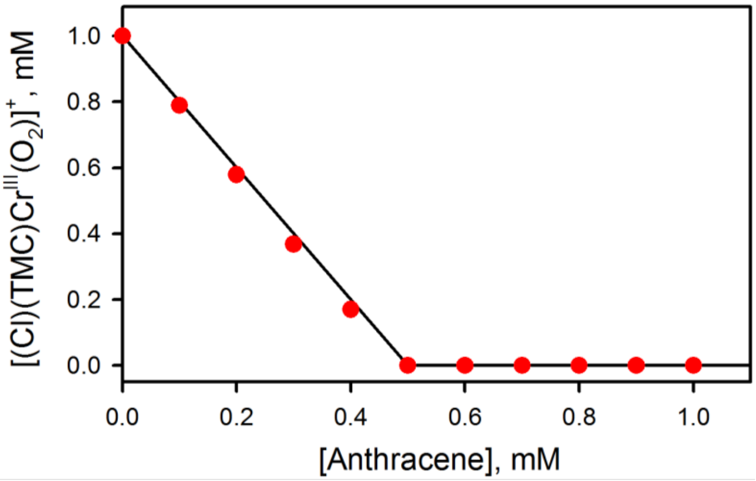


Fig. S2 Titration for the disappearance of **1** (red circles) as a function of the concentration of anthracene (0 – 1.0 mM) added to the solution of **1** (1.0 mM) in increments of 0.10 mM in the presence of HOTf (1.0 mM) in MeCN at 233 K.

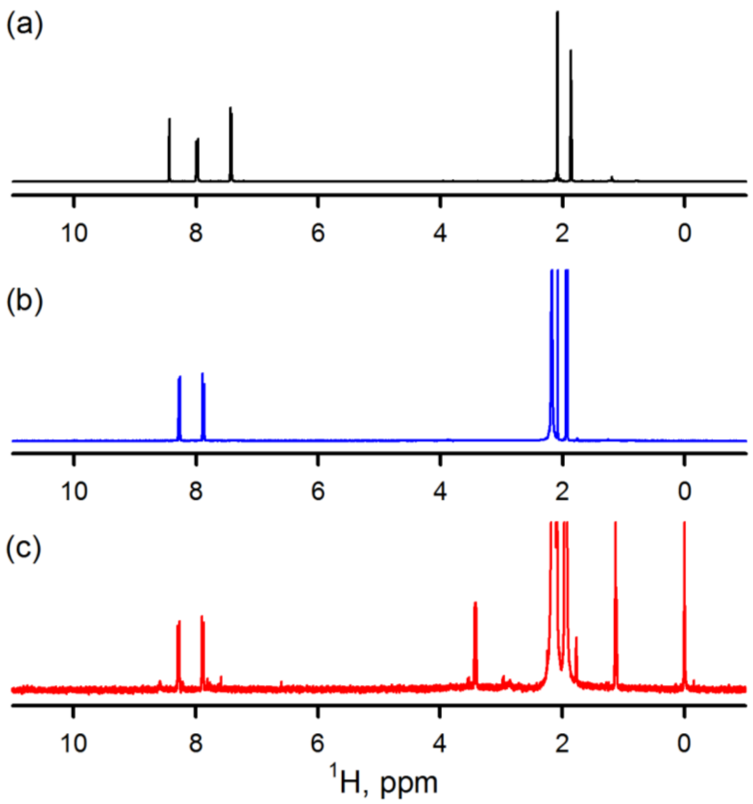


Fig. S3 ^{1}H NMR spectra of (a) anthracene (10 mM) and (b) anthraquinone (10 mM) as the authentic references, and (c) the reaction products obtained in the oxidation of anthracene (1.0 mM) by **1** (2.0 mM) in the presence of HOTf (2.0 mM) in MeCN-d_3 at 233 K.

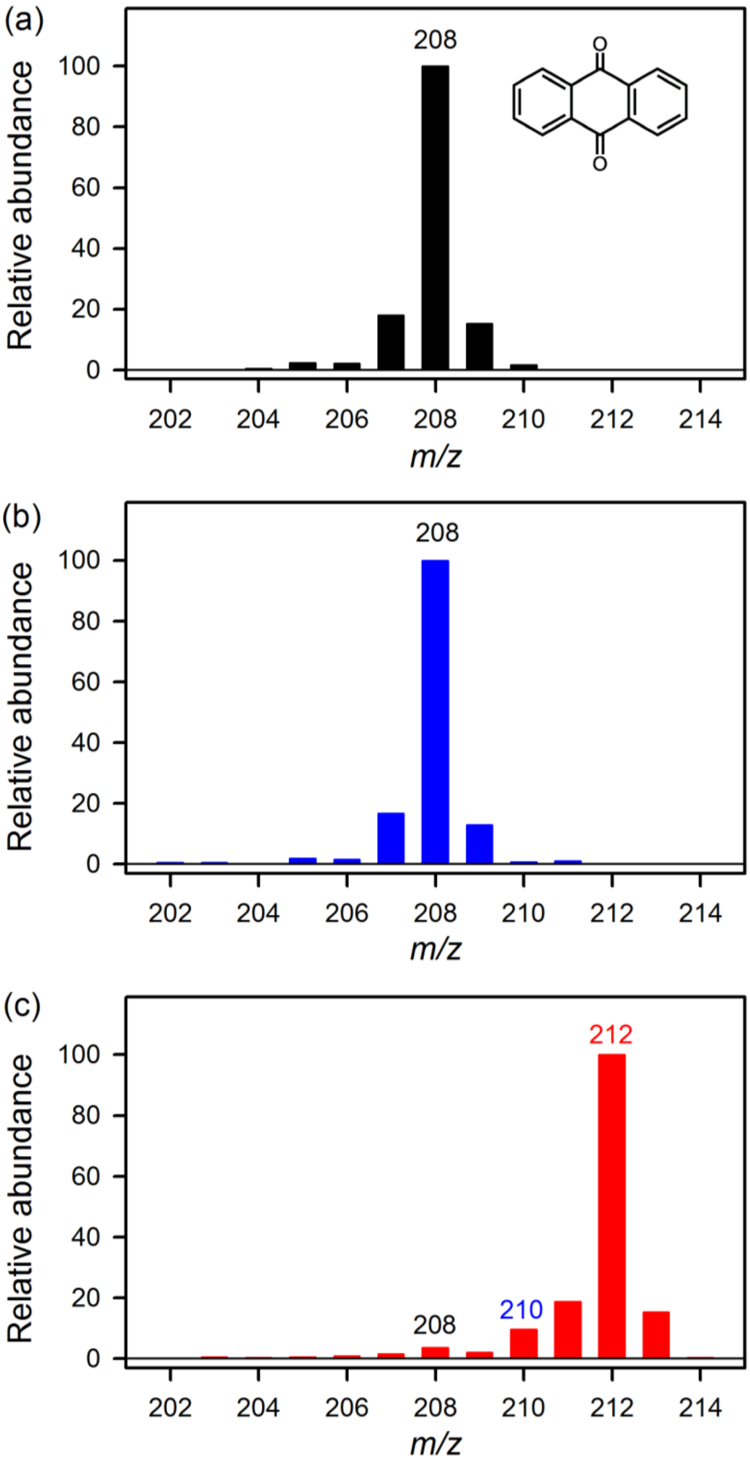


Fig. S4 GC-MS spectra of (a) anthraquinone (1.0 mM) as an authentic reference and (b, c) the reaction solutions obtained in the oxidation of anthracene (0.50 mM) by (b) **1**-$^{16}O_2$ (1.0 mM) and (c) **1**-$^{18}O_2$ (1.0 mM) in the presence of HOTf (1.0 mM) in MeCN at 233 K. The percentage of ^{18}O in anthraquinone product in (c) was determined to be 94(4)% by comparison of the relative abundances at m/z = 212 for anthraquinone-^{18}O,^{18}O, m/z = 210 for anthraquinone-^{16}O,^{18}O and m/z = 208 for anthraquinone-^{16}O,^{16}O.

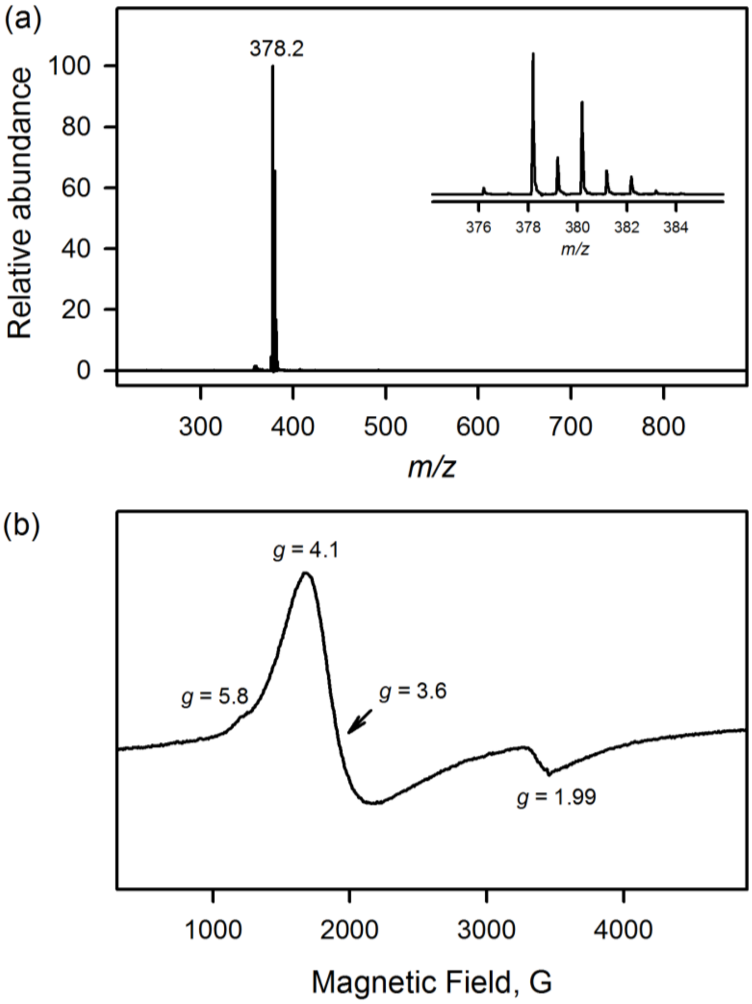


Fig. S5 (a) CSI-MS spectrum of the complete reaction solution obtained in the oxidation of anthracene (0.50 mM) by **1** (1.0 mM) in the presence of HOTf (1.0 mM) in MeCN at 233 K. The peak at *m/z* = 378.2 corresponds to $[Cr^{III}(TMC)(Cl_2)]^+$ (*calc. m/z* = 378.1). Inset shows the isotope distribution pattern of the peak at *m/z* = 378.2. (b) X-band EPR spectrum of the complete reaction solution obtained in the oxidation of anthracene (0.50 mM) by **1** (1.0 mM) in the presence of HOTf (1.0 mM) in MeCN at 233 K. The spectrum was recorded at 5 K.

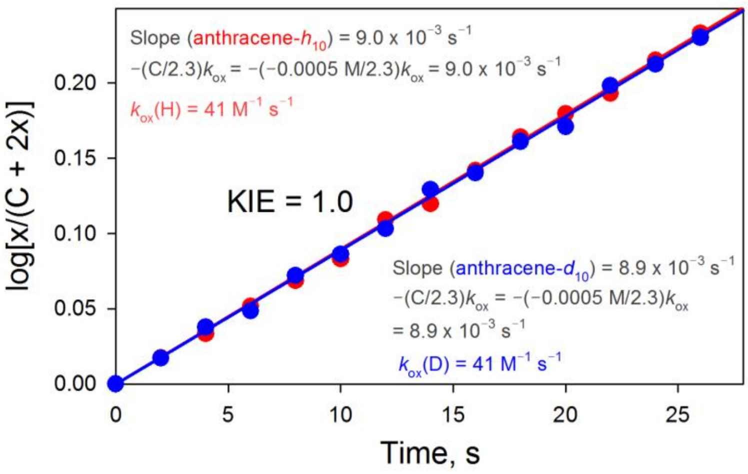


Fig. S6 Plots of log[x/(C + 2x)] *vs*. time for the oxidation of anthracene-h_{10} (0.50 mM; red circles) and anthracene-d_{10} (0.50 mM; blue circles) by **1** (0.50 mM) in the presence of HOTf (2.5 mM) in MeCN at 233 K. The k_{ox} values were determined by using $\log[x/(C + 2x)] = -(C/2.3)k_{ox}t + \log[x_0/(C + 2x_0)]$, where x = [**1**], x_0 = [**1**]$_0$, C = $-x_0$ = –[**1**]$_0$ and $x_0/(C + 2x_0) = 1$ [eqn (5) in text].

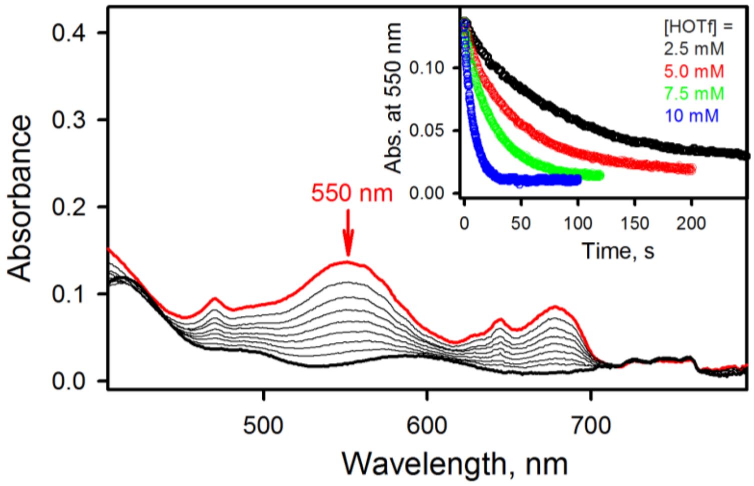


Fig. S7 UV-visible spectral changes observed in the oxidation of anthracene (0.50 mM) by **1** (0.50 mM) in the presence of HOTf (10 mM) in MeCN at 233 K. Inset shows the time profiles at 550 nm due to decay of **1** (0.50 mM) in the oxidation of anthracene (0.50 mM) by **1** in the presence of HOTf [2.5 mM (black), 5.0 mM (red), 7.5 mM (green) and 10 mM, (blue)] in MeCN at 233 K.

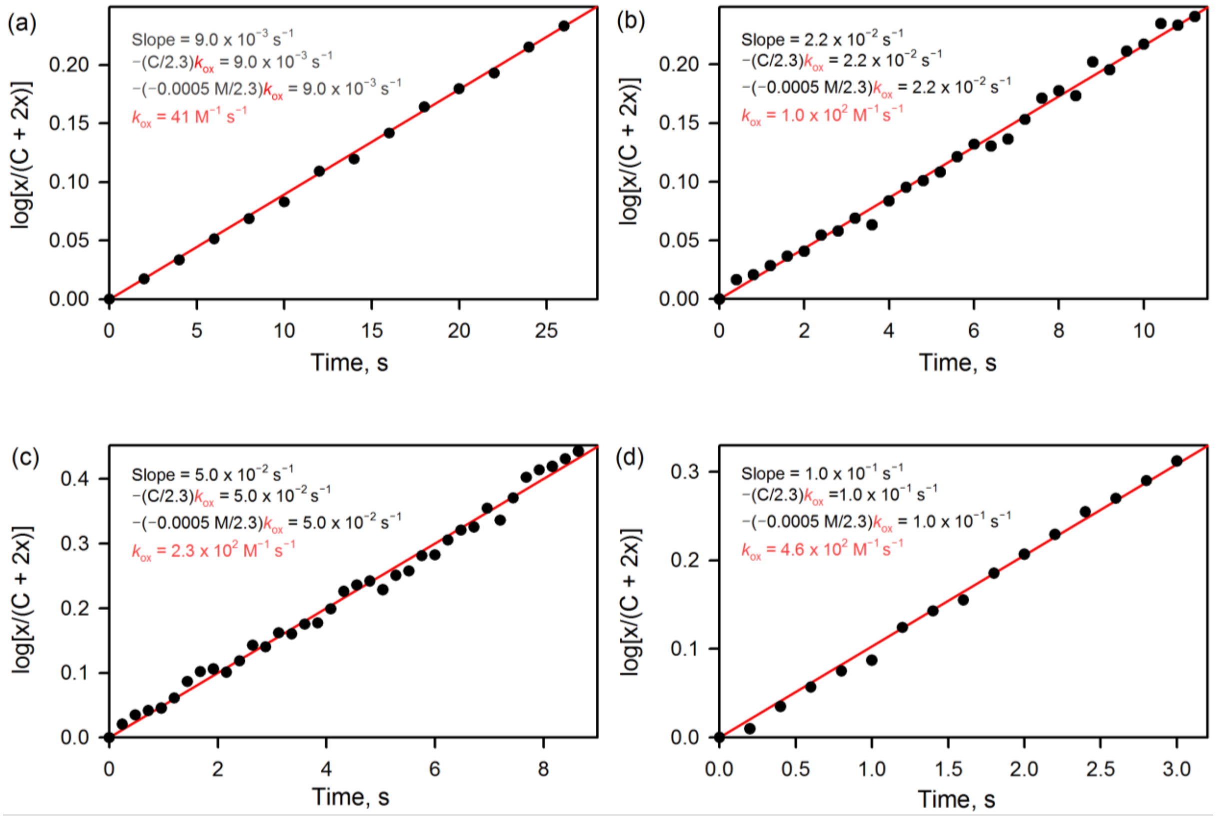


Fig. S8 Plots of log[x/(C+ 2x)] *vs*. time for the oxidation of anthracene (0.50 mM) by **1** (0.50 mM) in the presence of HOTf [(a) 2.5 mM, (b) 5.0 mM, (c) 7.5 mM and (d) 10 mM] in MeCN at 233 K. The k_{ox} values were determined by using $\log[x/(C + 2x)] = -(C/2.3)k_{ox}t + \log[x_0/(C + 2x_0)]$, where x = [**1**], x_0 = [**1**]$_0$, C = –[**1**]$_0$ and $x_0/(C + 2x_0) = 1$ [eqn (5) in text].

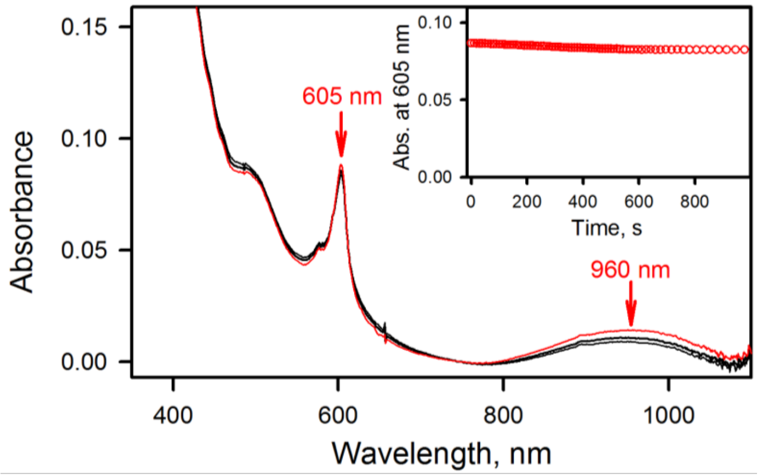


Fig. S9 UV-vis spectral changes observed in the oxidation of anthracene (0.50 mM) by $[Cr^{IV}(TMC)(O)]^{2+}$ (1.0 mM) in the presence of HOTf (2.5 mM) in MeCN at 233 K. The inset shows the time profile monitored at 605 nm due to the decay of $[Cr^{IV}(TMC)(O)]^{2+}$.

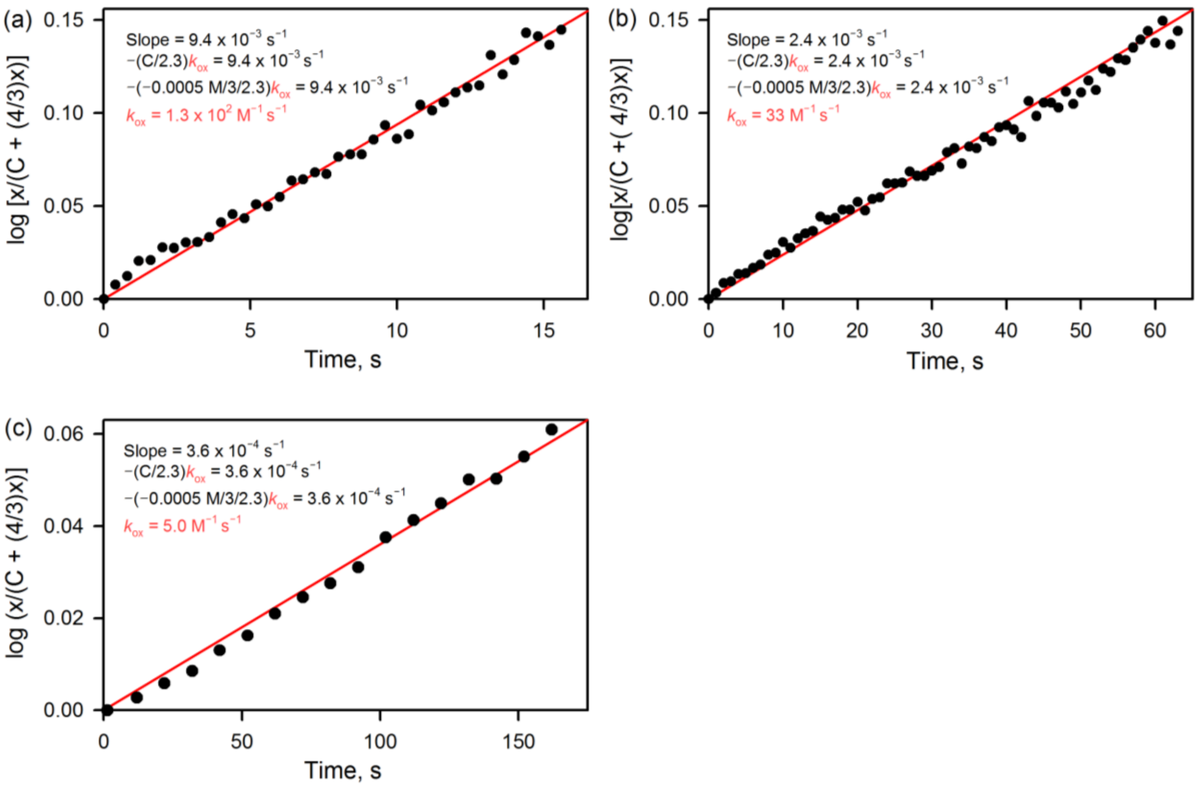


Fig. S10 Plots of log[x/(C + (4/3)x)] *vs*. time for the oxidation of (a) 9-methylanthracene (0.50 mM), (b) 9-bromoanthracene (0.50 mM) and (c) 9-anthracenecarboxaldehyde (0.50 mM) by **1** (0.50 mM) in the presence of HOTf (2.5 mM) in MeCN at 233 K. The k_{ox} values were determined by using log[x/(C + (4/3)x)] = –(C/2.3)$k_{ox}t$ + log [x_0/(C + (4/3)x_0)], where x = [**1**], x_0 = [**1**]$_0$, C = [XAn]$_0$ – (4/3)[**1**]$_0$ = –1/3[**1**]$_0$ and x_0/(C + (4/3)x_0) = 1 [eqn (S5) in ESI].

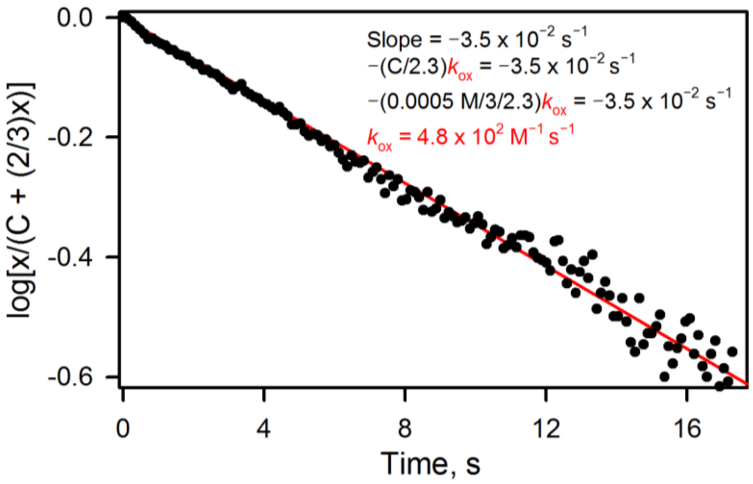


Fig. S11 Plot of log[x/(C + (2/3)x)] *vs*. time for the oxidation of 9,10-dimethylanthracene (0.50 mM) by **1** (0.50 mM) in the presence of HOTf (2.5 mM) in MeCN at 233 K. The k_{ox} values were determined by using log[x/(C + (2/3)x)] = –(C/2.3)$k_{ox}t$ + log[x_0/(C + (2/3)x_0)], where x = [**1**], x_0 = [**1**]$_0$, C = [XAn]$_0$ – (2/3)[**1**]$_0$ = 1/3[**1**]$_0$ and x_0/(C + (2/3)x_0) = 1 [eqn (S10) in ESI].