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Supporting Information

Copper(I)-based oxidation of polycyclic aromatic hydrocarbons and product elucidation using vacuum ultraviolet spectroscopy and theoretical spectral calculations

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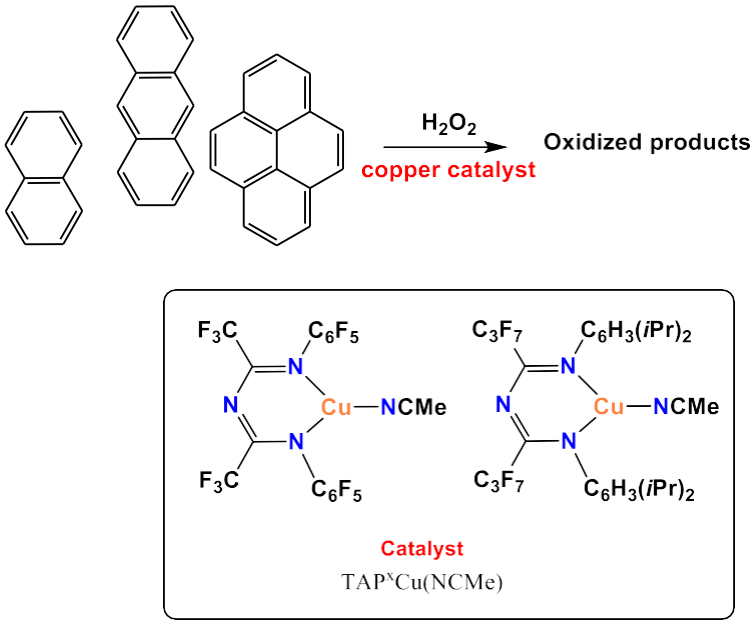


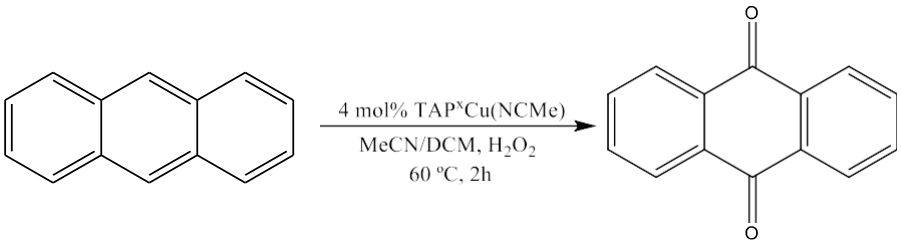
General Consideration

The NMR spectra were recorded at the room temperature on a JEOL Eclipse 500 spectrometer (^{1}H: 500.16 MHz). Proton chemical shifts are reported in ppm and are referenced using the residual proton signals of the deuterated solvent (^{1}H: $CDCl_3$, δ 7.26).

GC-VUV Data

A VGA-100 VUV detector (VUV Analytics, Inc., Cedar Park, TX) was coupled to a Shimadzu GC-2010 gas chromatograph (Shimadzu Scientific Instruments, Inc., Columbia, MD) and used to collect the data in this study. Chromatographic separation was carried out on a Rxi-5 column (30 m × 0.25 mm i.d. × 0.25 µm d_f; Restek). The injector temperature was set to 300 °C, a 0.5 µL injection volume was used, and the split ratio was 50:1. The carrier gas (He) was set to a constant linear velocity of 28 cm/s. The oven profile for the column was as follows: 100 °C (hold 2.0 min); ramp at 16 °C/min to 320 °C and hold for 10 min. The temperatures of the VUV transfer line and flow cell were thermostatted at 300 °C. The make-up gas (N_2) was 0.15 psi.

Oxidation of Anthracene



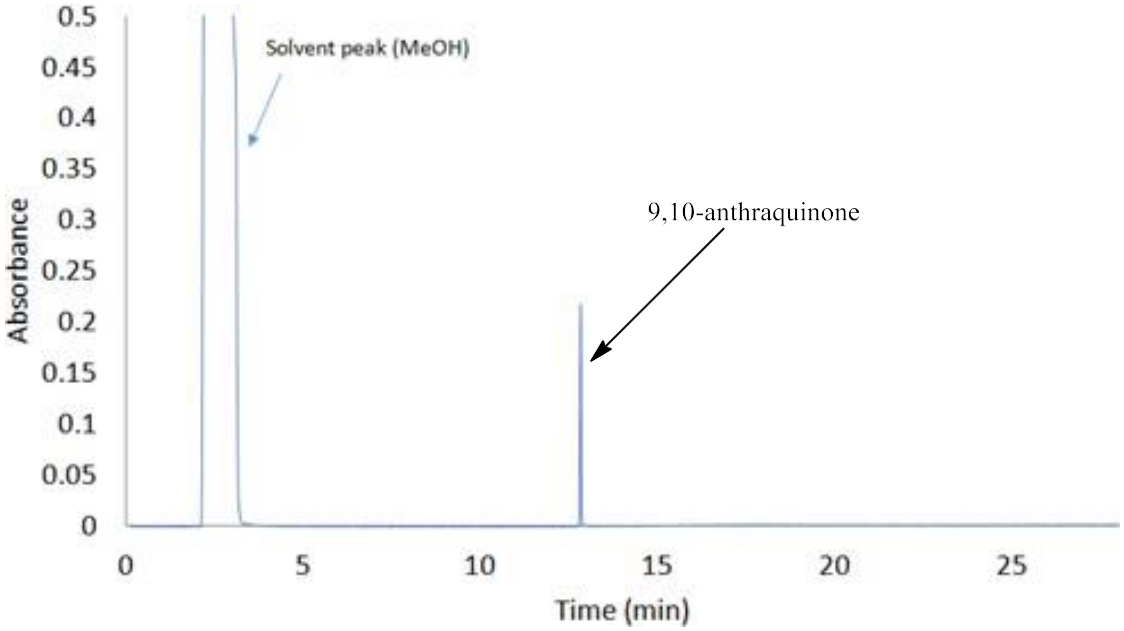


Figure S1. Chromatogram of anthracene oxidation products

Oxidation of Naphthalene

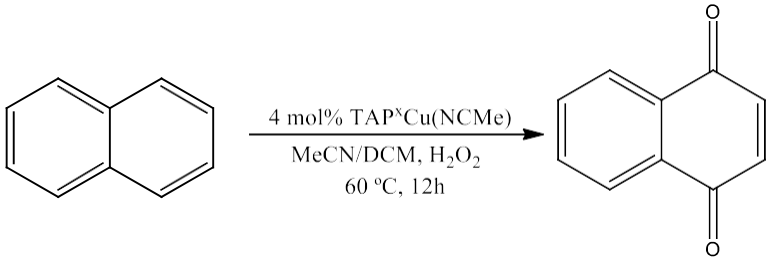


Table S1. Oxidation of naphthalene and the isolated yields of 1,4-napthoquinone (1,4-NQ)

Substrate	**Catalyst (mol%)**	**H_2O_2 (mmol.)**	**Temp (^oC)**	**Time (h)**	**Conversion (%)**	**Isolated Yields (%) 1,4-NQ**
Naphthalene	$[N\{(CF_3)C(C_6F_5)N\}_2]CuNCCH_3$ (4%)	15	60	12	64	19*
Naphthalene	$[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ (4%)	15	60	12	52	14

*GC yield = 21%

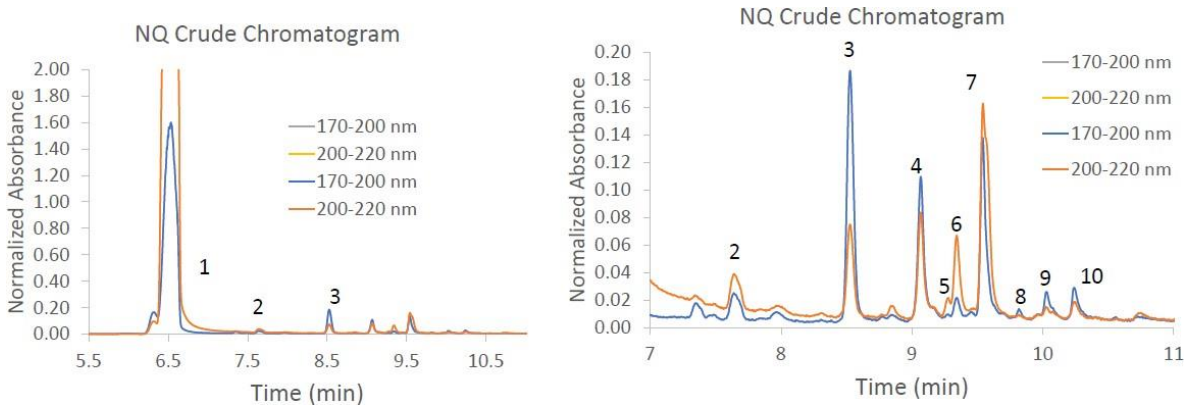


Figure S2. Chromatogram of naphthalene oxidation products (*peaks 3, 5 and 6 were identified as 1,4-naphthoquinone, 1-, and 2-naphthol, respectively using computational and VUV data).*

Oxidation of Pyrene

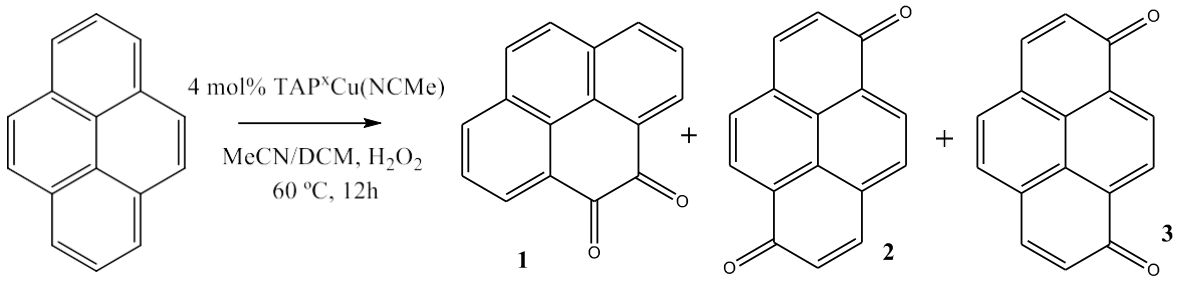


Table S2. Oxidation of pyrene and the yields of 4,5-, 1,6-, and 1,8-pyrenequinones (**1, 2,** and **3**, respectively)

Substrate	Catalyst (mol%)	H_2O_2 (mmol.)	Temp (^{O}C)	Time (h)	Conv. (%)	Isolated Yields (%) 4,5-, 1,6- and 1,8-pyrenequinones, 1, 2, 3
Pyrene	$[N\{(CF_3)C(C_6F_5)N\}_2]CuNCCH_3$ (4%)	15	60	12	40.5	4 (**1**), 5 (**2**), 7 (**3**)
Pyrene	$[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ (4%)	15	60	12	50.2	6 (**1**), 9 (**2**), 12 (**3**)
Pyrene	$[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ (6%)	15	60	12	59-60	7 (**1**), 11 (**2**), 16 (**3**)
Pyrene	$[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ (10%)	15	60	12	43	5 (**1**), 9 (**2**), 11 (**3**)

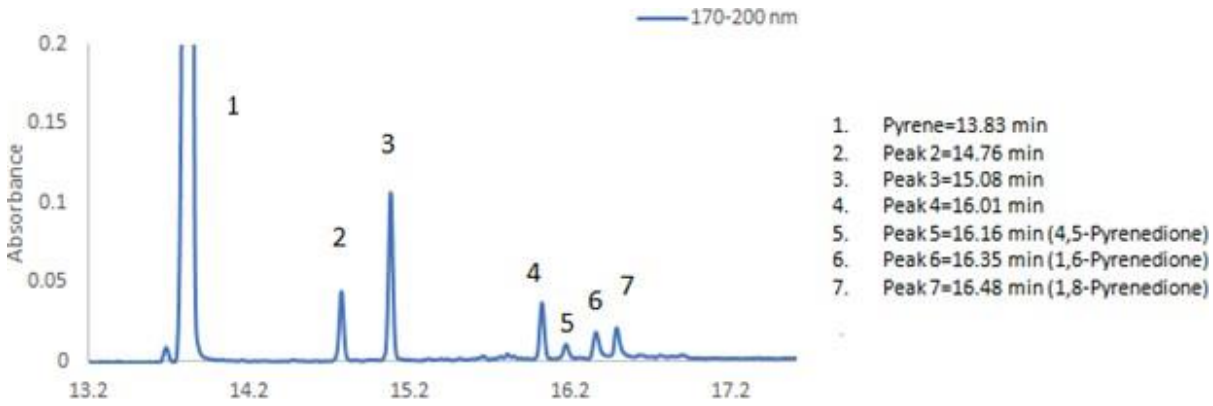
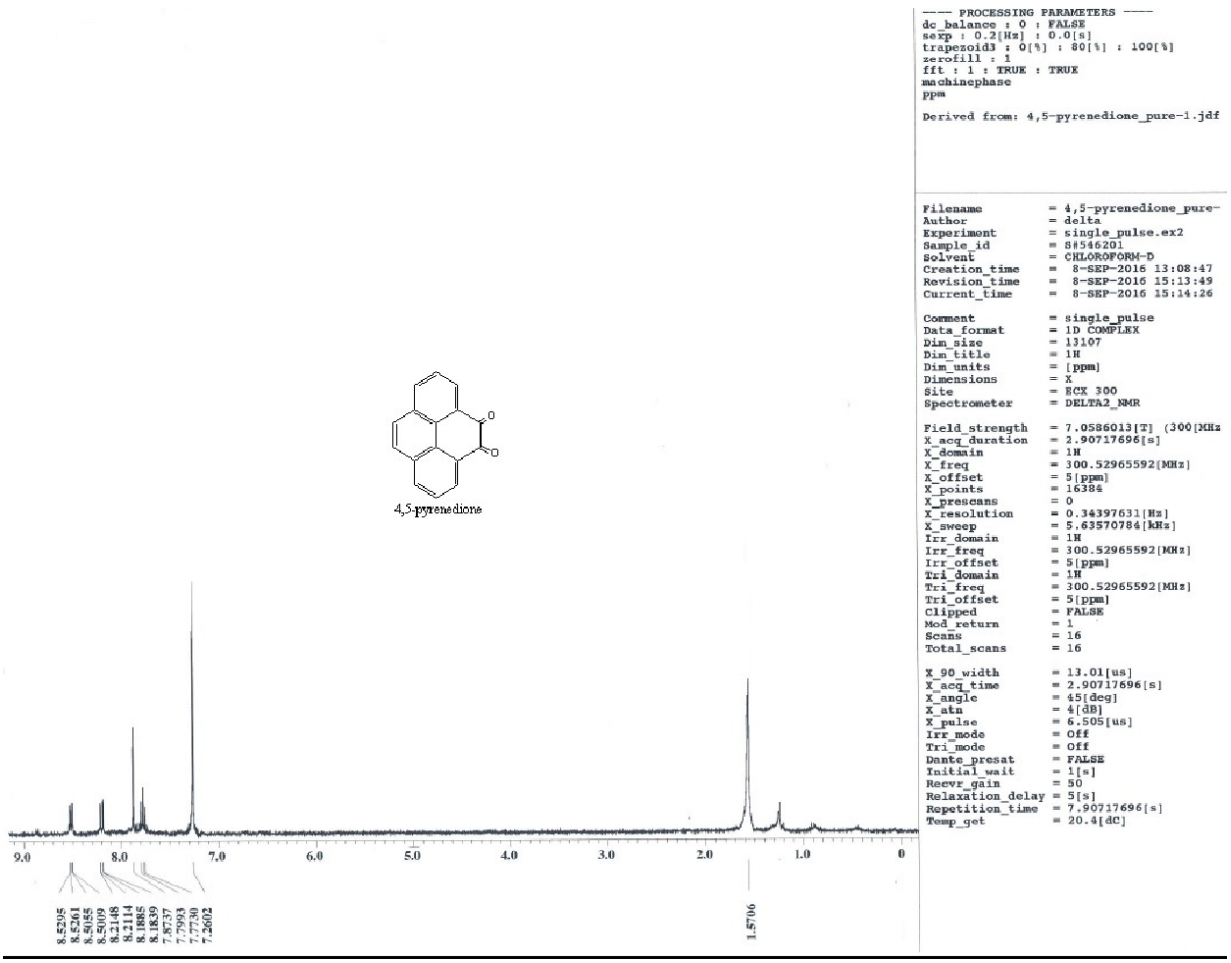


Figure S3. Chromatogram of pyrene oxidation products

^{1}H NMR Spectra of 1, 2, and 3

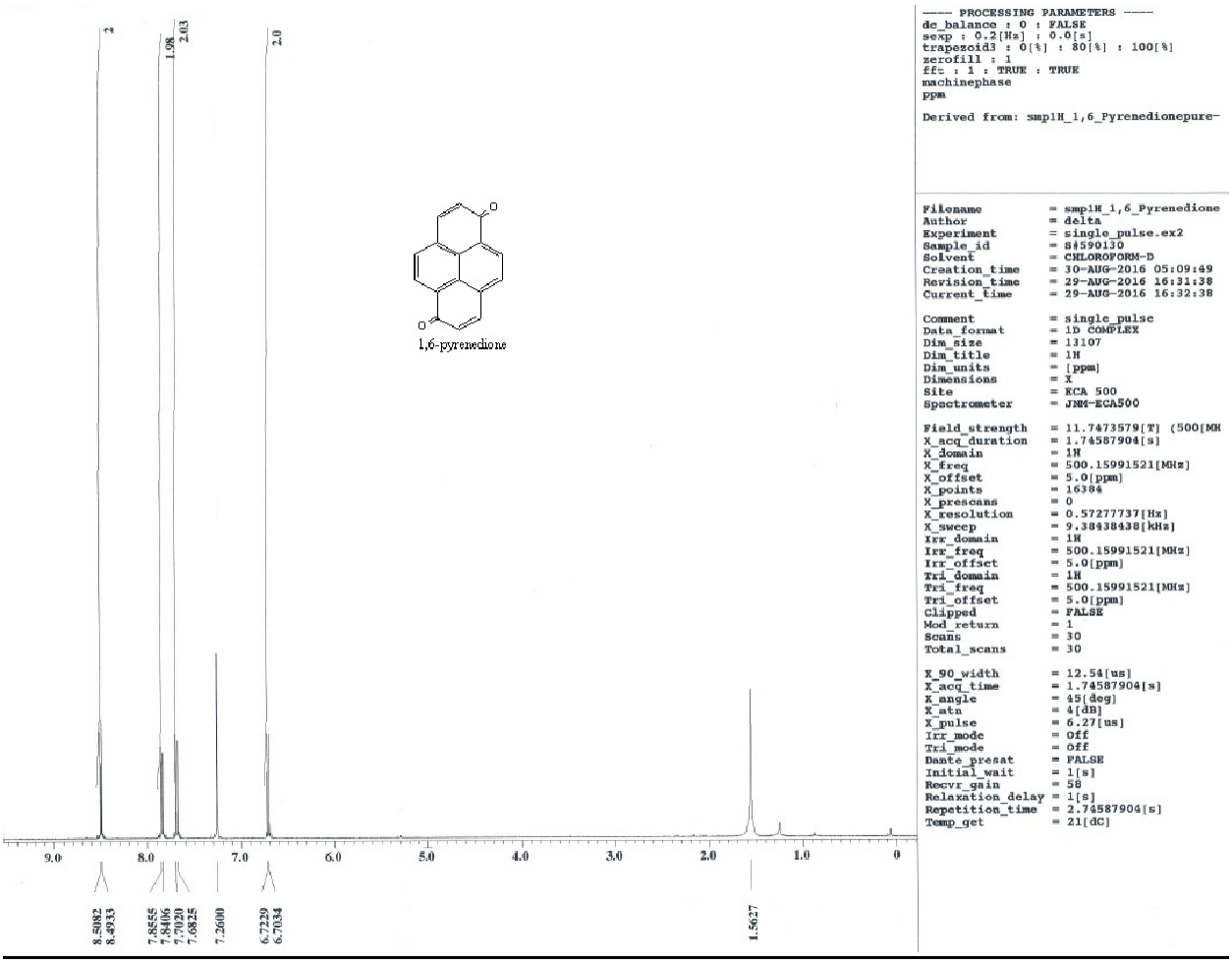
4,5-Pyrenedione (1)[1]

^{1}H NMR (500.16 MHz, $CDCl_3$) δ 8.51 (dd, J = 1.7 Hz, J = 7.2 Hz, 2H), 8.19 (dd, J = 1.7 Hz, J = 7.2 Hz, 2H), 7.87 (s, 2H), 7.78 (t, J = 7.5 Hz, 2H)



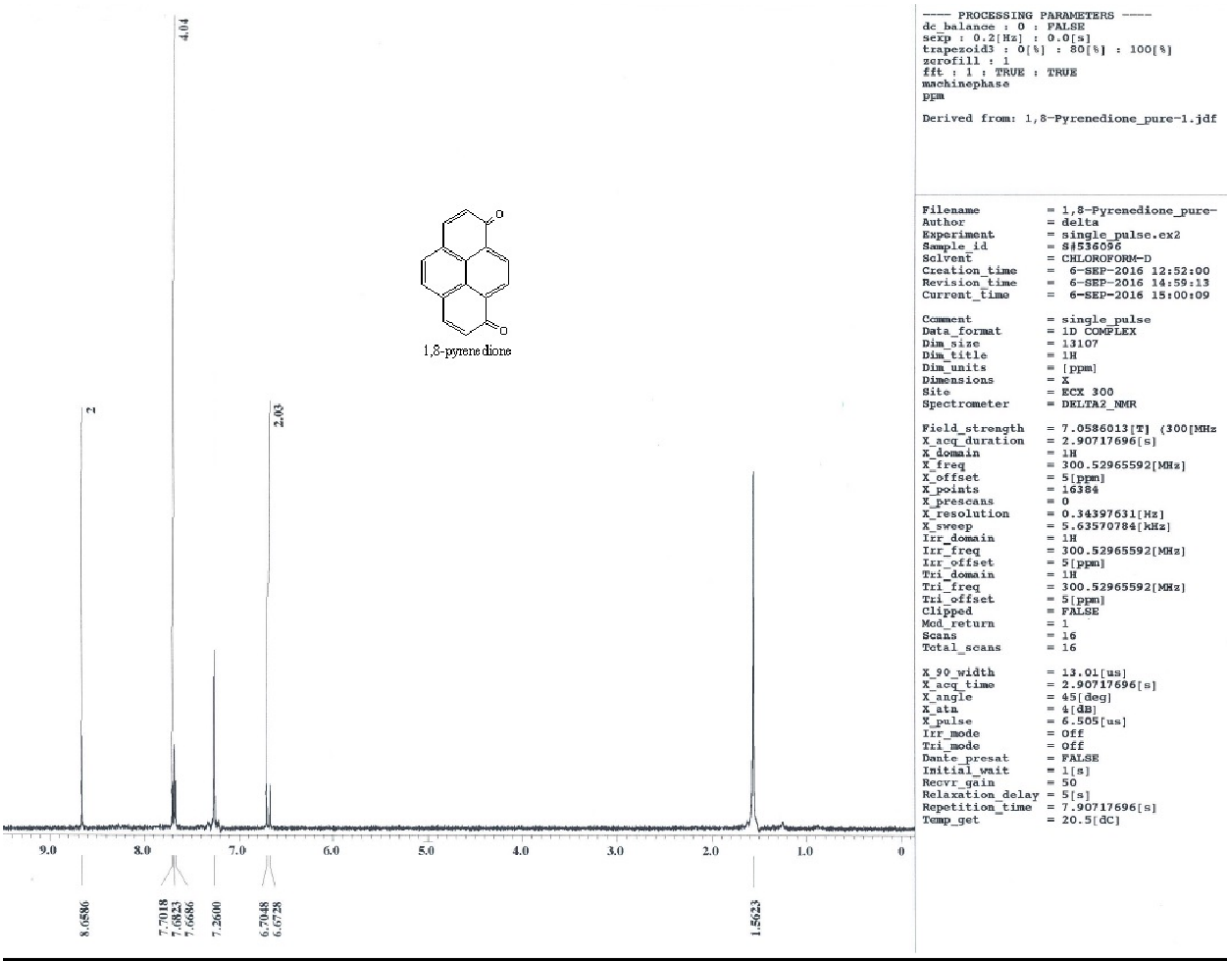
1,6-Pyrenedione (2)[2]

^{1}H NMR (500.16 MHz, $CDCl_3$) δ 8.49 (d, J = 7.5 Hz, 2H), 7.84 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 9.8 Hz, 2H), 6.71 (d, J = 9.8 Hz, 2H)



1,8-Pyrenedione (3)[2]

^{1}H NMR (500.16 MHz, $CDCl_3$) δ 8.65 (s, 2H), 7.69 (d, 2H, J = 9.8 Hz), 7.66 (s, 2H), 6.68 (d, 2H, J = 9.8 Hz).



Theoretical computations method

Theoretical VUV absorption spectra were calculated using time-dependent density functional theory (TDDFT)[3] with B3LYP functionals[4-7] and 6-31 þ G(d,p)[8, 9] basis set at each molecules' optimized B3LYP/6- 31 þ G(d,p) geometries. All calculations were performed using Gaussian 09 program (version A.02)[10] at High Performance Computing at University of Texas at Arlington. A full-width half maximum (FWHM) of 0.4 eV and a shifting factor of 0.99 were used to generate computed spectra for calculation of sum-squared residues (SSR) with corresponding experimental spectra.

In order to identify an analyte, standard spectral analysis normally requires the pre-existence of the pure analyte spectra in a searchable database library. Although the VUV library is developing quickly (~2000 compounds currently), there are situations where the desired spectra of some structures have not been measured and are therefore unavailable in the library. In these cases, we are exploring the solution of using reliable theoretical spectra generated by computational chemistry to substitute experimental spectra. This solution has produced quite satisfactory results in a previous study.[11]

In this study, several possible oxidation products' experimental VUV spectra were un-available in the library. To speculate these oxidation products' structures, a computational method was employed, as follows: The structures of feasible oxidation products were derived by common sense of chemistry first; and the VUV spectra of these structures were then calculated using an established computational chemistry method (TDDFT).[3] The observed experimental VUV spectra of each oxidation product were compared with these calculated spectra. The structure whose calculated spectrum matches the experimental spectrum best (indicated by smallest sum of squared residuals) was assigned as the most possible structure.

We have showed in our previous study that this procedure usually is capable to pick up the correct structure.[11] To further testify the validity of this method, for all compounds in this study whose VUV spectra are available in the library, their VUV spectra were calculated and compared with their experimental counterparts first. All SSRs were shown less than 50.

X-ray crystallography:

Table S3. Crystal data and structure refinement for **[N{(CF$_3$)C(C$_6$F$_5$)N}$_2$]CuNCCH$_3$**.

Identification code	rad369_0m_a
Empirical formula	$C_{18}H_3CuF_{16}N_4$
Formula weight	642.78
Temperature/K	298.5
Crystal system	triclinic
Space group	P-1
a/Å	8.802(2)
b/Å	9.701(2)
c/Å	13.814(3)
α/°	103.683(8)
β/°	90.251(9)
γ/°	107.230(8)
Volume/Å^3	1091.1(4)
Z	2
ρ_{calc}g/cm^3	1.957
μ/mm^{-1}	1.153
F(000)	624.0
Crystal size/mm^3	0.3 × 0.17 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.526 to 54.998
Index ranges	$-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-17 \leq l \leq 17$
Reflections collected	18600
Independent reflections	4990 [R_{int} = 0.0475, R_{sigma} = 0.0311]
Data/restraints/parameters	4990/0/353
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0424, wR_2 = 0.1266
Final R indexes [all data]	R_1 = 0.0561, wR_2 = 0.1376
Largest diff. peak/hole / e Å^{-3}	0.66/-0.57

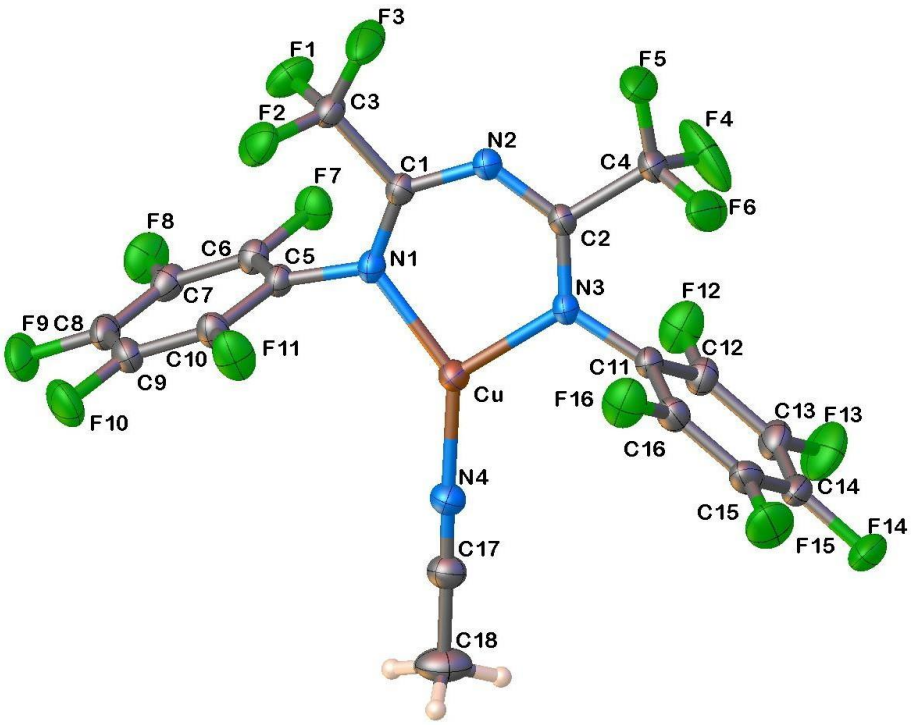


Table S4. Bond Lengths for $[N\{(CF_3)C(C_6F_5)N\}_2]CuNCCH_3$.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu	N1	1.948(2)	N2	C1	1.335(3)
Cu	N3	1.977(2)	N2	C2	1.332(3)
Cu	N4	1.854(3)	N3	C2	1.295(3)
F1	C3	1.317(3)	N3	C11	1.417(3)
F2	C3	1.329(3)	N4	C17	1.127(4)
F3	C3	1.292(3)	C1	C3	1.542(3)
F4	C4	1.283(4)	C2	C4	1.546(3)
F5	C4	1.293(4)	C5	C6	1.389(3)
F6	C4	1.323(4)	C5	C10	1.392(3)
F7	C6	1.339(3)	C6	C7	1.381(4)
F8	C7	1.332(3)	C7	C8	1.368(4)
F9	C8	1.339(3)	C8	C9	1.366(4)
F10	C9	1.342(3)	C9	C10	1.375(4)
F11	C10	1.332(3)	C11	C12	1.385(4)
F12	C12	1.335(3)	C11	C16	1.379(4)
F13	C13	1.331(4)	C12	C13	1.381(4)
F14	C14	1.342(3)	C13	C14	1.359(5)
F15	C15	1.343(4)	C14	C15	1.369(5)

F16	C16	1.331(4)	C15	C16	1.380(4)
N1	C1	1.295(3)	C17	C18	1.436(5)
N1	C5	1.417(3)			

Table S5. Bond Angles for $[N\{(CF_3)C(C_6F_5)N\}_2]CuNCCH_3$.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
N1	Cu	N3	94.31(9)	F7	C6	C7	119.0(2)
N4	Cu	N1	138.57(10)	C7	C6	C5	121.9(2)
N4	Cu	N3	127.06(10)	F8	C7	C6	119.6(3)
C1	N1	Cu	121.24(16)	F8	C7	C8	120.5(3)
C1	N1	C5	123.5(2)	C8	C7	C6	119.9(2)
C5	N1	Cu	115.21(16)	F9	C8	C7	120.3(3)
C2	N2	C1	124.9(2)	F9	C8	C9	119.8(3)
C2	N3	Cu	121.08(16)	C9	C8	C7	119.9(2)
C2	N3	C11	124.2(2)	F10	C9	C8	119.7(3)
C11	N3	Cu	114.59(16)	F10	C9	C10	120.3(3)
C17	N4	Cu	175.3(3)	C8	C9	C10	120.0(3)
N1	C1	N2	129.0(2)	F11	C10	C5	118.8(2)
N1	C1	C3	120.1(2)	F11	C10	C9	119.2(2)
N2	C1	C3	110.9(2)	C9	C10	C5	122.0(2)
N2	C2	C4	111.2(2)	C12	C11	N3	121.1(2)
N3	C2	N2	128.5(2)	C16	C11	N3	121.1(2)
N3	C2	C4	120.3(2)	C16	C11	C12	117.3(2)
F1	C3	F2	104.8(2)	F12	C12	C11	119.4(2)
F1	C3	C1	111.5(2)	F12	C12	C13	118.7(3)
F2	C3	C1	110.8(2)	C13	C12	C11	121.9(3)
F3	C3	F1	109.2(3)	F13	C13	C12	120.2(3)
F3	C3	F2	106.5(3)	F13	C13	C14	120.4(3)
F3	C3	C1	113.6(2)	C14	C13	C12	119.4(3)
F4	C4	F5	109.7(3)	F14	C14	C13	119.7(4)
F4	C4	F6	104.5(3)	F14	C14	C15	120.2(3)
F4	C4	C2	111.3(3)	C13	C14	C15	120.1(3)
F5	C4	F6	104.3(3)	F15	C15	C14	120.3(3)
F5	C4	C2	114.1(2)	F15	C15	C16	119.3(3)
F6	C4	C2	112.4(2)	C14	C15	C16	120.3(3)
C6	C5	N1	121.4(2)	F16	C16	C11	118.9(3)
C6	C5	C10	116.3(2)	F16	C16	C15	120.1(3)
C10	C5	N1	121.7(2)	C11	C16	C15	121.0(3)
F7	C6	C5	119.1(2)	N4	C17	C18	178.9(4)

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