Supplementary Information

"Turn-on" Fluorescent Probe for Highly Selective Discrimination of Hypochlorite (ClO⁻) from Oxidants including Dichromate (Cr₂O₇²⁻) in Aqueous Media

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CONTENTS

1. NMR Spectra

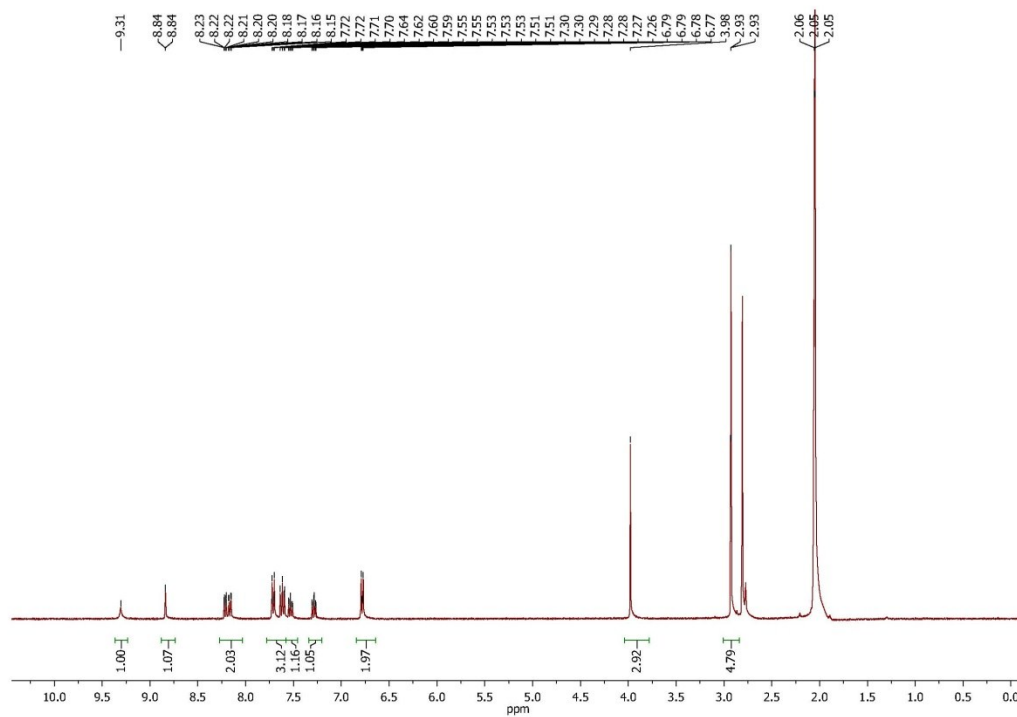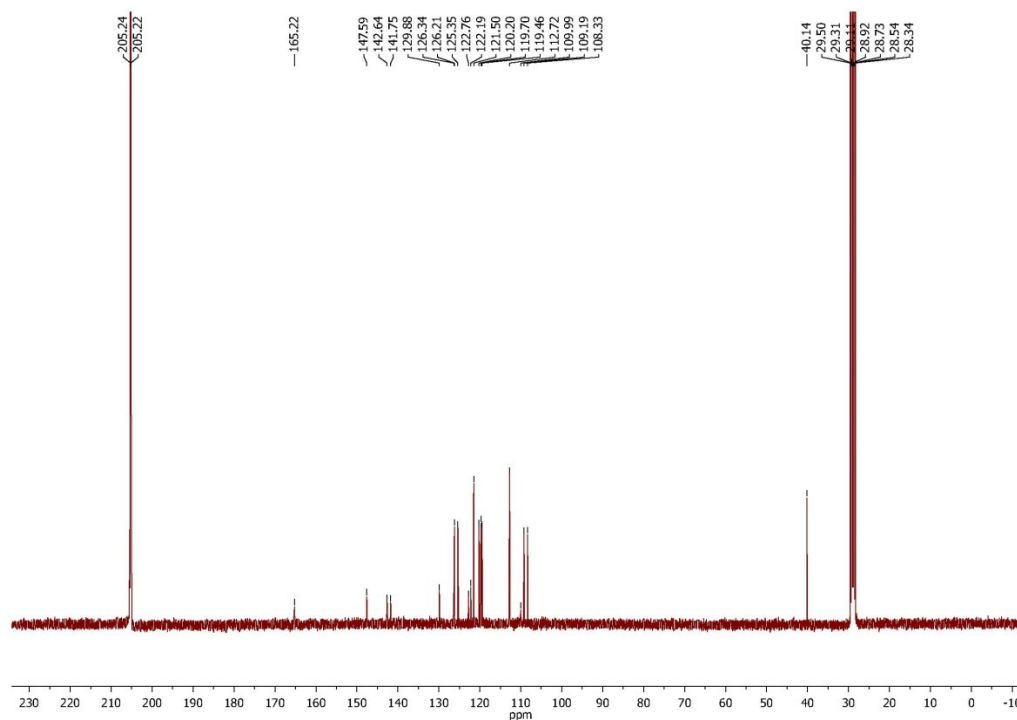**Figure S1-1.** ^{1}H NMR spectrum of **P1** in d_6-acetone.

Figure S1-2. ^{13}C NMR spectrum of **P1** in d_6-acetone.

2. Fluorescent Quantum Yield Determination

Anthracene was used as a standard for the quantum yield measurement of **P1**. Typically, the quantum yield was obtained by integrating the photons emitted by **P1** up to 600 nm and calculated using the following formula:[1]

$$\Phi_u = \Phi_s \frac{A_s F_u n^2}{A_u F_s n_0^2}$$

where A refers to absorbance at the excitation wavelength, F refers to integrated emission area across the band, Φ refers to quantum yield, n is refraction index of the solvent containing the unknown (n_0, standard), subscript u refers to "unknown", and subscript s refers to "standard".
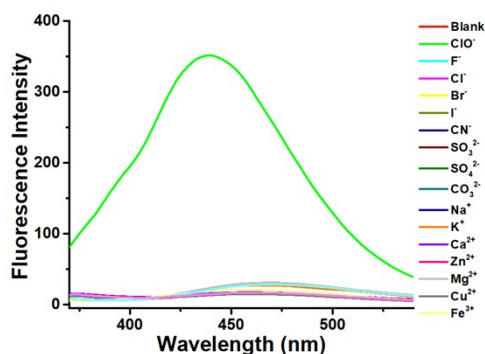

Figure S2-1. Emission spectra recorded for **P1** (2 μM) (slit width = 5 nm; λ_{ex} = 280 nm) after the addition of an anions and cations (indicated) at pH 7.4 (10 mM aqueous phosphate buffer).

3. NMR Studies

10 mM solutions of **P1** were independently prepared in d_6-acetone with 10% D_2O and d_6-acetone, respectively. Afterward, known quantities of $KMnO_4$ or NaClO were added and kept for a specified length of time after vigorous shaking. The resulting NaClO solutions were directly scanned at 298 K while the $KMnO_4$ resultants were filtered to remove precipitated manganese species before data acquisition.

4. Absorption Studies

UV-Vis spectroscopy samples were prepared in a similar manner as those described in the fluorescence titration section using an optical path length of 10 mm.
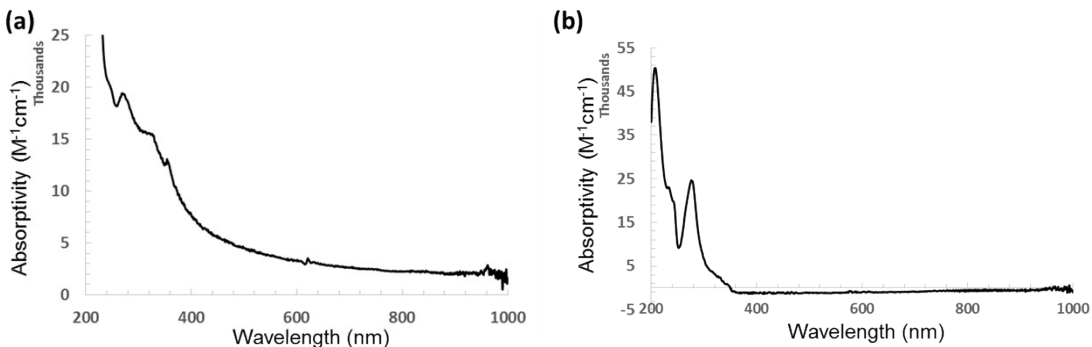
Figure S2-2. Absorption spectra of **P1** in 10 mM phosphate buffer (pH 7.4) **(a)**, and after oxidation by ClO⁻ **(b).**

5. Electrochemical Studies

Cyclic voltammetry (CV) of 0.5 mM of **P1** in 75% acetone with 25% water were performed using 5 mM of tetrabutylammonium dihydrogen phosphate (TBAH$_2$PO$_4$) as the supporting electrolyte. Various scan rates were applied. Platinum wire was used as working electrode, Ag/AgCl in 3 M NaCl (aq) was used as reference electrode, and carbon was used as the counter electrode.

6. Mass Spectrometry

Data were recorded for a solution of 2 μM of **P1** in THF before and after the addition of 20 equiv. of ~ 5% NaClO$_{(aq)}$.
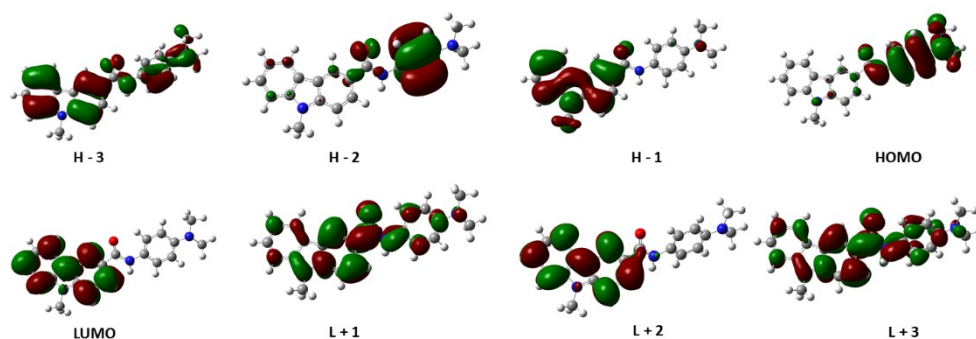
7. Calculations

The electronic structure calculations for **P1**, and its respective oxidation products were performed with the Gaussian09 program package.[2] The ground state geometries and electronic structures of the complexes were optimized at the CAM-B3LYP/6-311++G(d,p) level. Time-dependent density functional theory (TD-DFT) calculations were used to determine the optical properties of the complexes based on the S$_0$ ground-state geometry. All Gaussian calculations were performed with polarizable continuum model (solvent = water) to account for solvent effects. Gas-phase calculation of absorbance and fluorescence spectra for immediate comparison with experimental values were performed by Orca[3] program package.

Table S3-1. Calculated singlet excitation energies, oscillator strengths, and molecular orbitals (MOs) involved in the excitation for **P1**.

Energy/eV[a]	Wavelength/nm	Oscillator strength	MOs	Coefficient[b]
4.21	294.7	0.0343	H-1 → L+2	0.19406
			H → L+1	0.60349
			L → L+1	0.23983
4.35	285.0	1.1052	H-3 → L+2	0.10556
			H → L+2	0.22327
			L → L+2	0.59308
			L → L+9	0.10823
			L → L+15	0.10032
4.41	281.3	0.0554	L → L+6	0.61007
			L → L+8	0.26354
4.80	269.6	0.1979	H-1 → L+1	0.49426
			H → L+2	0.35220

[a]Only selected excited states were considered. [b]Configuration interaction (CI) coefficients are in absolute value.

Figure S3-1. Calculated molecular orbitals of **P1** based on the ground state geometries.

Table S3-2. Calculated singlet excitation energies, oscillator strengths, and molecular orbitals (MOs) involved in the excitation for [**P1**-p-2e]$^+$.

Energy/eV[a]	Wavelength/nm	Oscillator strength	MOs	Coefficient[b]
2.69	460.4	0.0116	H → L	0.64667
			H-1 → L	0.16686
			H-2 → L	0.15240
			H-3 → L	0.10435
3.94	314.4	0.0623	H-4 → L	0.14934
			H-6 → L	0.67502
4.05	306.0	1.3218	H-7 → L	0.10108
			H-6 → L	0.17891
			H-4 → L	0.40320
			H-3 → L	0.26558
			H-1 → L+1	0.12404
			H → L+2	0.40459
4.34	285.4	0.0676	H-7 → L	0.10544
			H-4 → L	0.21232
			H-3 → L	0.15508
			H-1 → L+1	0.27453
			H-1 → L+2	0.22382
			H → L+1	0.44309
			H → L+2	0.21254
4.52	274.5	0.2379	H-8 → L	0.12101
			H-7 → L	0.52160
			H-4 → L	0.16763
			H-4 → L+1	0.10863
			H-3 → L+1	0.29928

[a] Only selected excited states were considered. [b] The CI coefficients are represented as their absolute values.

[1] D. F. Eaton, *Pure Appl. Chem.,* 1988, **60**, 1107.
[2] Gaussian 09, Revision **E.01**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
[3] F. Neese, *Wires Comput. Mol. Sci.,* 2012, **2**, 73.