

Electronic Supplementary Information (ESI)

**A colorimetric and fluorescent turn-on sensor for pyrophosphate
anion based on dicyanomethylene-4*H*-chromene framework**

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General Information.

All solvents were of analytical grade. The intermediates of 2-(2-methyl-4*H*-chromen-4-ylidene)malononitrile and 4-[bis(pyridin-2-yl-methyl)amino]benzaldehyde were prepared by the established literature procedure.^[1,2] ¹H NMR and ¹³C NMR in CDCl₃ or DMSO-*d*₆ were measured on a Bruker AV-400 spectrometer with tetramethylsilane (TMS) as internal standard. Mass spectra were measured on a Micromass LCT. UV-vis spectra were obtained using a Varian Cary 500 spectrophotometer (1 cm quartz cell) at 25 °C. Fluorescent spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer (1 cm quartz cell) at 25 °C

2-(4-(bis(pyridin-2-ylmethyl)amino)styryl)-4*H*-chromen-4-ylidene)malononitrile (DCCP)

2-(2-methyl-4*H*-chromen-4-ylidene)malononitrile (0.38 g, 1.83 mmol) and 4-[bis(pyridine-2-yl-methyl)amino]benzaldehyde (0.50 g, 1.65 mmol) were both dissolved in toluene (30 ml) with piperidine (0.2 ml) and acetic acid (0.4 ml) under argon protection at room temperature. Then the mixture was refluxed and stirred for 12 h. The solvent was evaporated in vacuo. The crude solid was purified by column chromatography on silica gel eluting with petroleum ether / ethyl acetate (1/ 1, v / v) to afford a purple solid in 48% yield. ¹H-NMR δ (400 MHz, CDCl₃): 4.91 (s, 4H), 6.57 (d, *J* = 15.6 Hz, 1H), 6.79 (m, 3H), 7.23 (m, 4H), 7.43 (m, 3H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.54 (d, *J* = 15.6 Hz, 1H), 7.68 (m, 3H), 8.63 (d, *J* = 4.8 Hz, 2H), 8.92 (d, *J* = 8.4 Hz, 1H). ¹³C-NMR δ (100 MHz, CDCl₃): 57.16, 60.70, 105.51, 112.82, 113.77, 116.21, 117.29, 117.94, 118.45, 120.79, 122.39, 123.76, 125.65, 125.73, 130.00,

134.24, 136.98, 139.36, 149.90, 150.43, 152.35, 152.78, 157.70, 158.62. HRMS (ESI) calcd for $C_{32}H_{23}N_5O$ [$M^+ + H$] 494.1981, found 494.1971.

DCCP-Cu²⁺

The aqueous solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.24 g, 0.65 mmol) was added dropwise to DCCP (0.15 g, 0.31 mmol) in 25 mL MeOH and the mixture was stirred for 24 h at room temperature, then the precipitate was filtered and washed with cold water to give DCCP-Cu²⁺ (0.15g, 64 %) as a brown powder. MS (ESI) calcd for $C_{32}H_{23}CuN_5O$ [$M+Cu^{2+}-H^+$] 556.10, found 556.14. IR: (KBr, disc): $\nu = 3432, 2913, 2362, 2212, 1633, 1598, 1558, 1505, 1481, 1456, 1408, 1259, 1120, 1097, 773, 620, 549\text{ cm}^{-1}$.

References

- [1] G. G. Badcock, F. M. Dean, A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 1950, 903.
- [2] X. Peng, J. Du, J. Fan, J. Wang, Y. Wu, J. Zhao, S. Sun and T. Xu, *J. Am. Chem. Soc.*, 2007, **129**, 1500.

Table S1. Association constants for binding of competitive ions to DCCP determined by UV/vis titration in a mixture of ethanol-water (60 : 40, v / v) with a buffer solution of MOPS (10 mM, pH = 7.0).

Metal ions	Cu ²⁺	Zn ²⁺	Ni ²⁺
K _{ass}	1.1(2) × 10 ⁶	5.7(9) × 10 ⁴	1.65(5) × 10 ⁴

Note: Cu²⁺ showed stronger binding affinity, almost two magnitudes higher than Zn²⁺ and Ni²⁺, which might be result in the slight change in the emission spectra of DCCP with the titration of Zn²⁺.

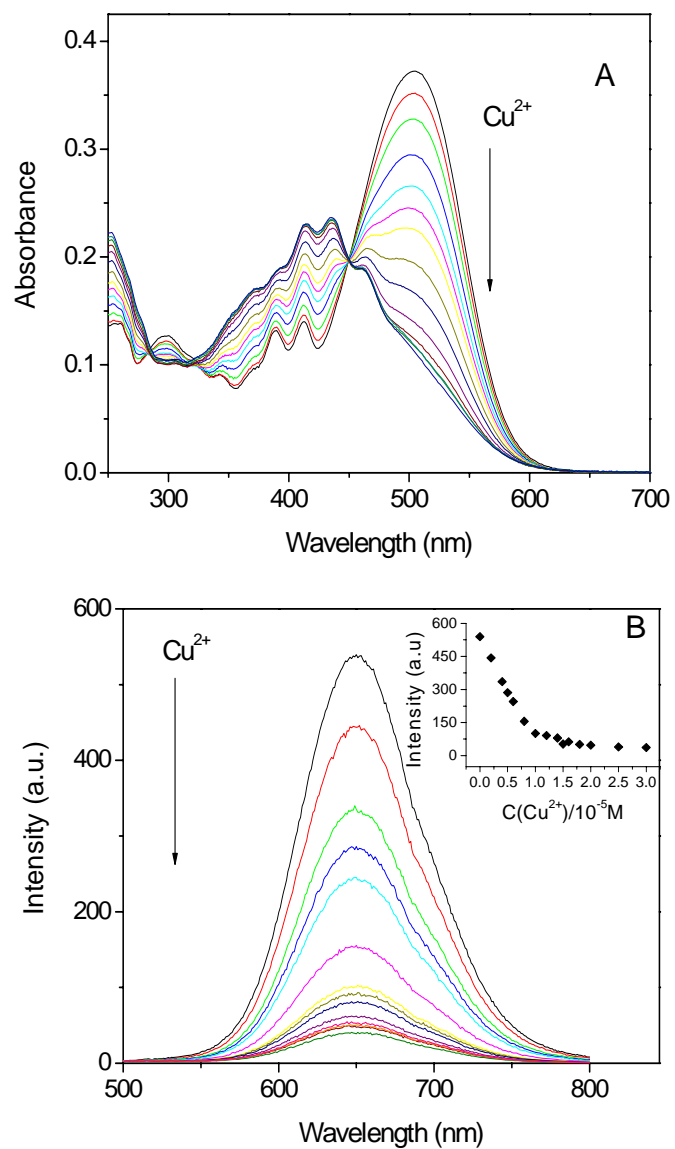


Figure S1. Absorption spectra (A) and emission spectra (B) of DCCP (10 μM) with excitation wavelength of 447 nm in a mixture of ethanol-water (60 : 40, v / v) with a buffer solution of MOPS (10 mM, pH = 7.0) upon titration of Cu²⁺ (0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.5, 1.6, 1.8, 2.0, 3.0, 5.0 equiv).

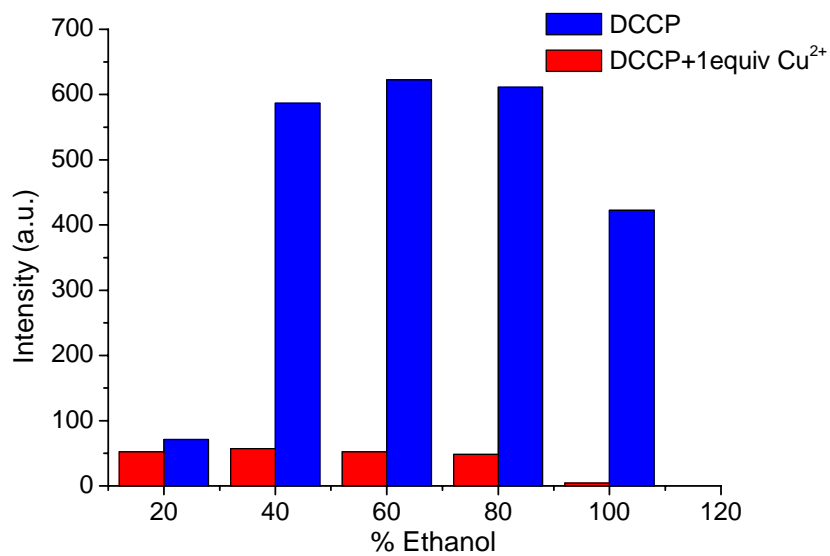


Figure S2. Effects of water composition on the fluorescence of (a) only DCCP; (b) DCCP in the presence of 1 equiv of Cu²⁺.

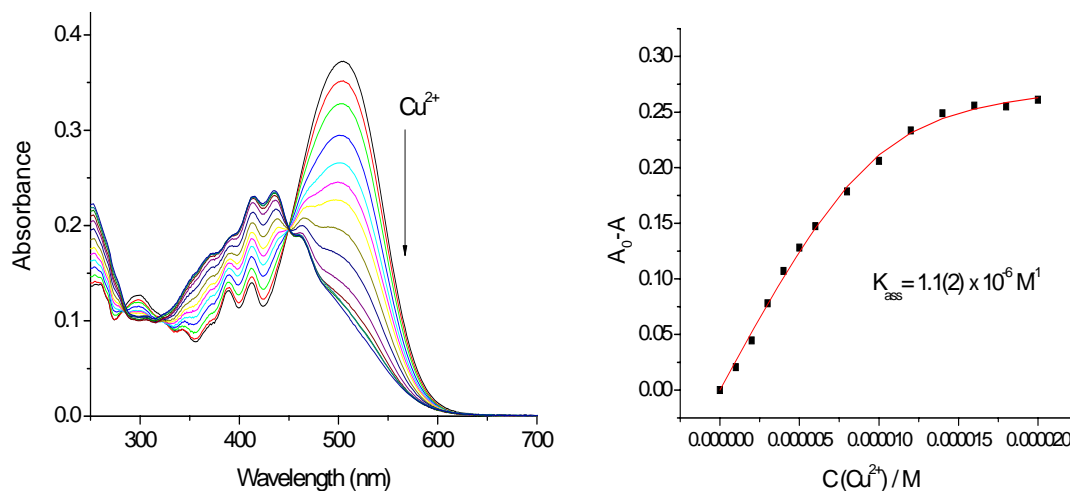


Figure S3. Electronic spectra changes during the titration of 10 μM DCCP with CuCl_2 in a mixture of ethanol-water (60 : 40, v / v) with a buffer solution of MOPS (10 mM, pH = 7.0) (left) and the corresponding data fitting to saturation curve (right).

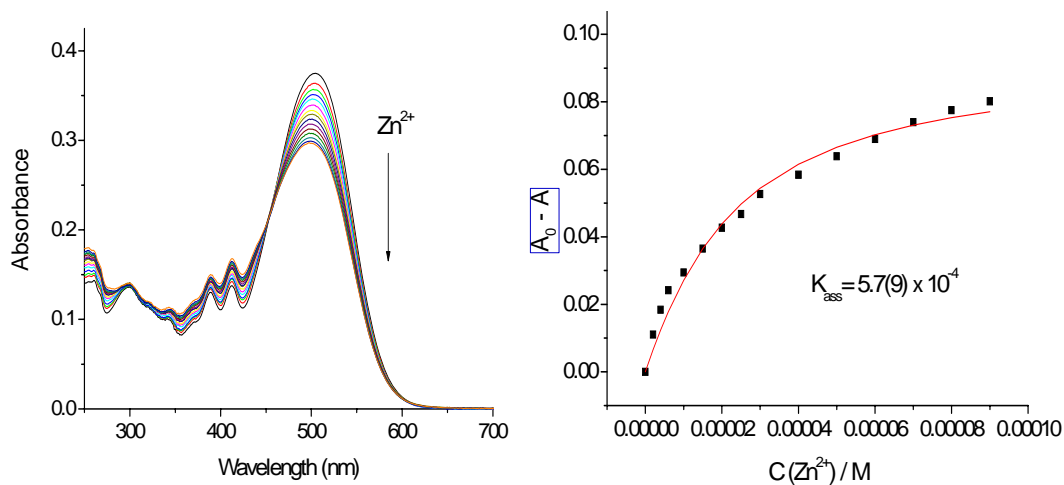


Figure S4. Electronic spectra changes during the titration of 10 μM DCCP with ZnCl_2 in a mixture of ethanol-water (60 : 40, v / v) with a buffer solution of MOPS (10 mM, pH = 7.0) (left) and the corresponding data fitting to saturation curve (right).

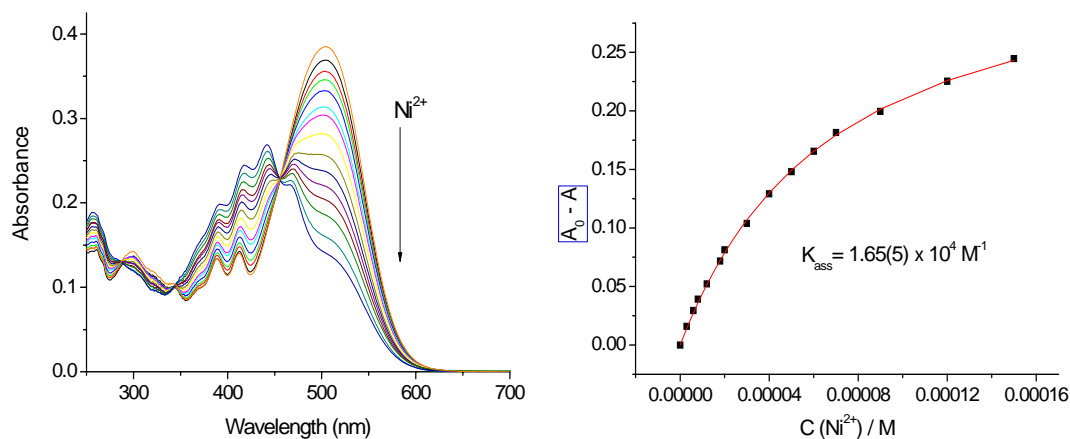


Figure S5. Electronic spectra changes during the titration of 10 μM DCCP with NiCl₂ in a mixture of ethanol-water (60 : 40, v / v) with a buffer solution of MOPS (10 mM, pH = 7.0) (left) and the corresponding data fitting to saturation curve (right).

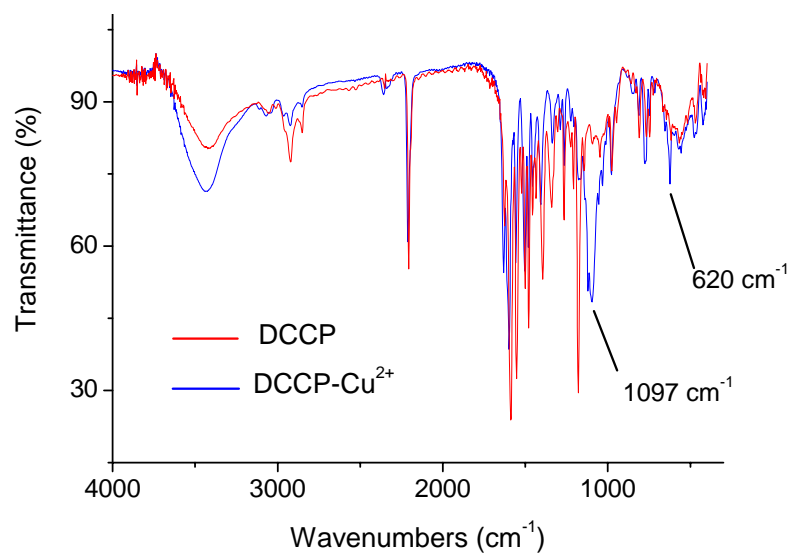


Figure S6. IR spectra of DCCP and DCCP-Cu²⁺. Note: the peaks at 1097 and 620 cm⁻¹ in infra-red (IR) spectra corresponding to the characteristic vibration of ClO₄⁻ also confirms the complex formation of DCCP-Cu²⁺.

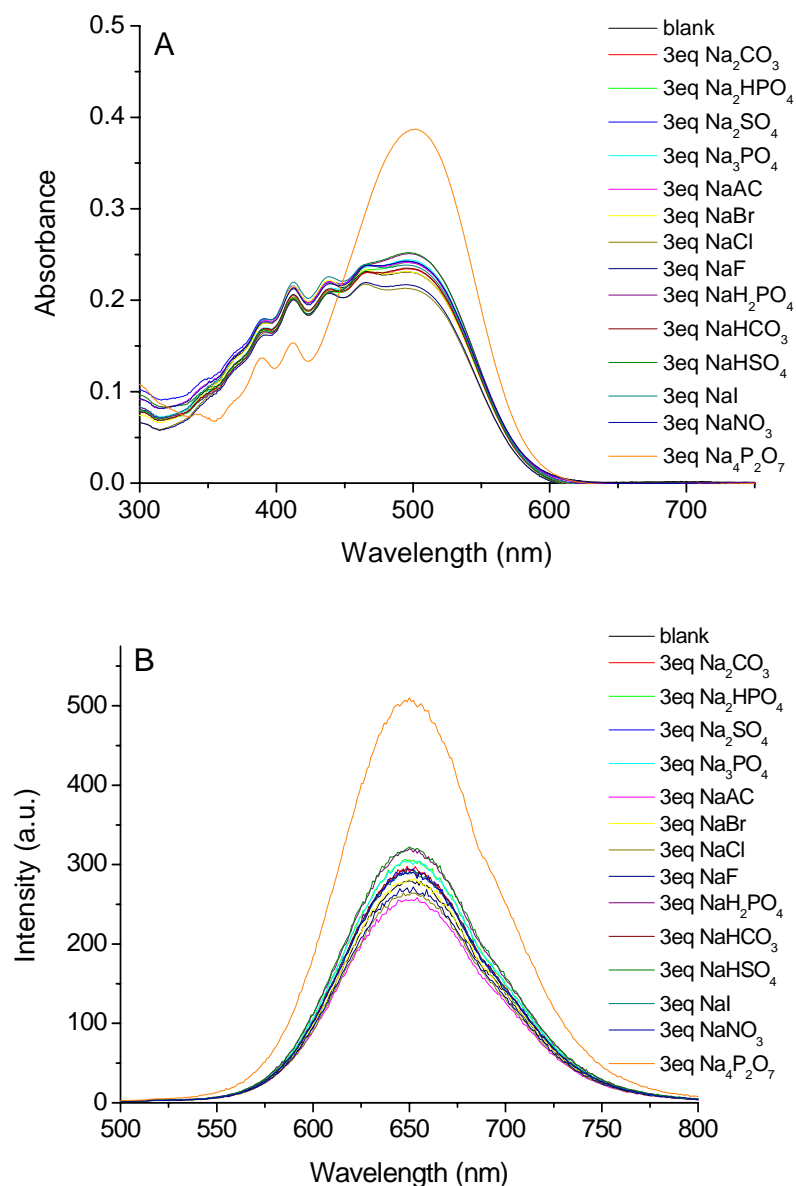


Figure S7. Absorption spectra (A) and emission spectra (B) of DCCP-Cu²⁺ with excitation wavelength of 447 nm (isobestic point) in ethanol-water solutions (60:40, v/v, 10 mM MOPS buffer, pH 7.0) in the presence of different anions (F⁻, Cl⁻, Br⁻, I⁻, H₂PO₄⁻, HCO₃⁻, HSO₄⁻, CH₃COO⁻, NO₃⁻, HPO₄²⁻, SO₄²⁻, CO₃²⁻, PO₄³⁻, P₂O₇⁴⁻). The concentration of DCCP-Cu²⁺ was 10 μM and the concentration of each anions was 30 μM.

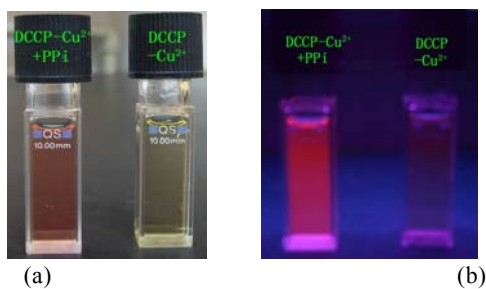


Figure S8. Photographic images observed from DCCP-Cu²⁺ with the addition of PPI anions ($[DCCP-Cu^{2+}] = 10 \mu M$, $[PPI] = 10 \mu M$): (a) color change; (b) fluorescent emission change irradiated at 365 nm by a portable fluorescent lamp.

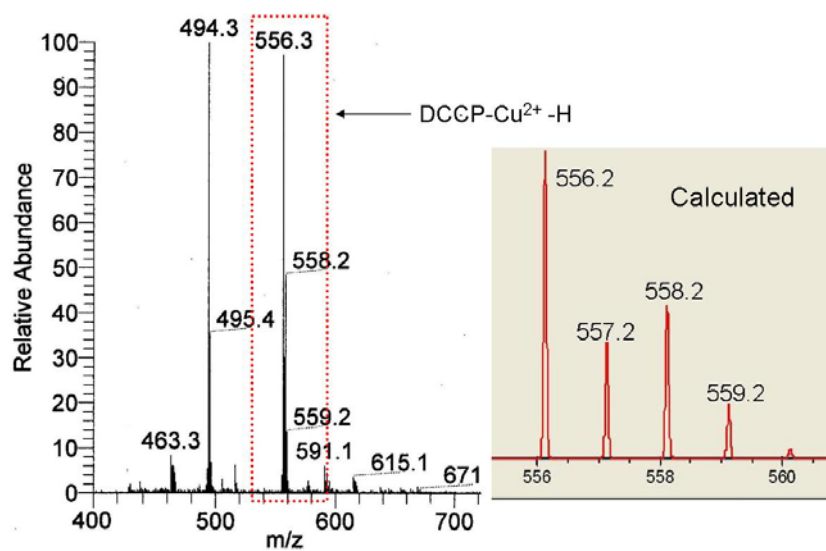


Figure S9. Portion ESI mass spectra of DCCP-Cu²⁺ upon the addition of excess PPI (100 equiv). Right: calculated isotopic patterns for the DCCP-Cu²⁺.

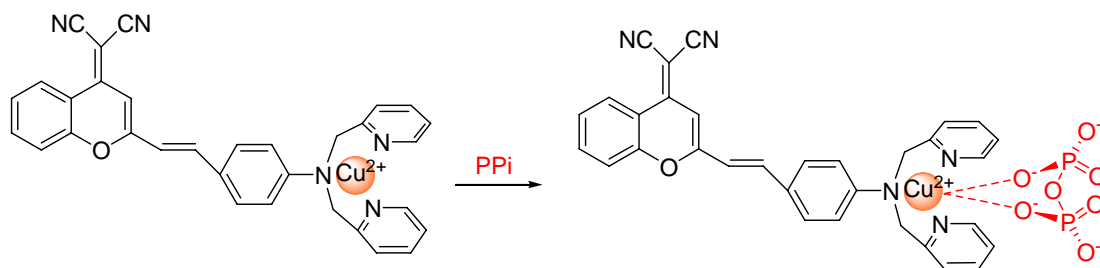


Figure S10. Proposed coordination of pyrophosphate anion with DCCP-Cu²⁺ resulting in the fluorescence enhancement.

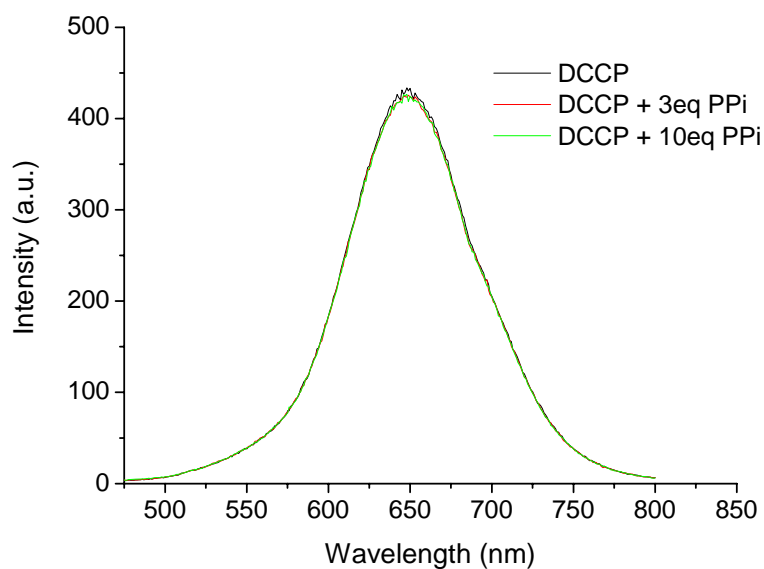


Figure S11. Emission spectra of DCCP (10 μM) upon titration with PPi in a mixture of ethanol-water (60 : 40, v / v) with a buffer solution of MOPS (10 mM, pH = 7.0), indicating that pyrophosphate anion has weak or no effect on the ligand fluorescence of DCCP.

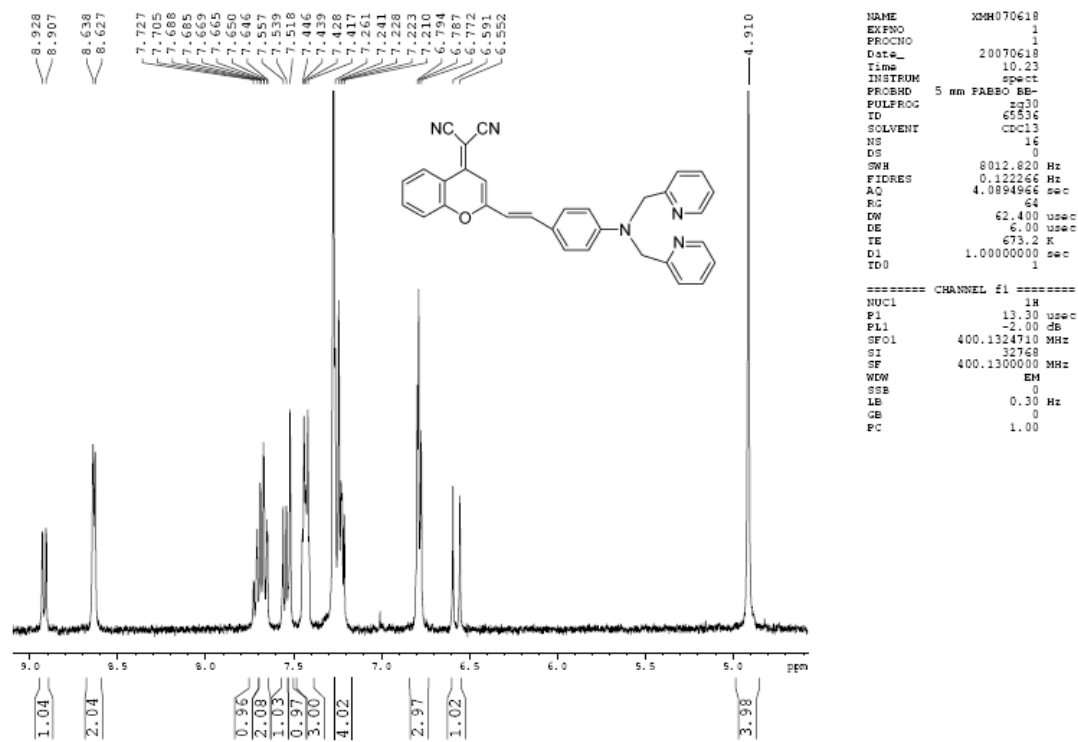


Figure S12. ¹H-NMR spectra of DCCP in CDCl₃.

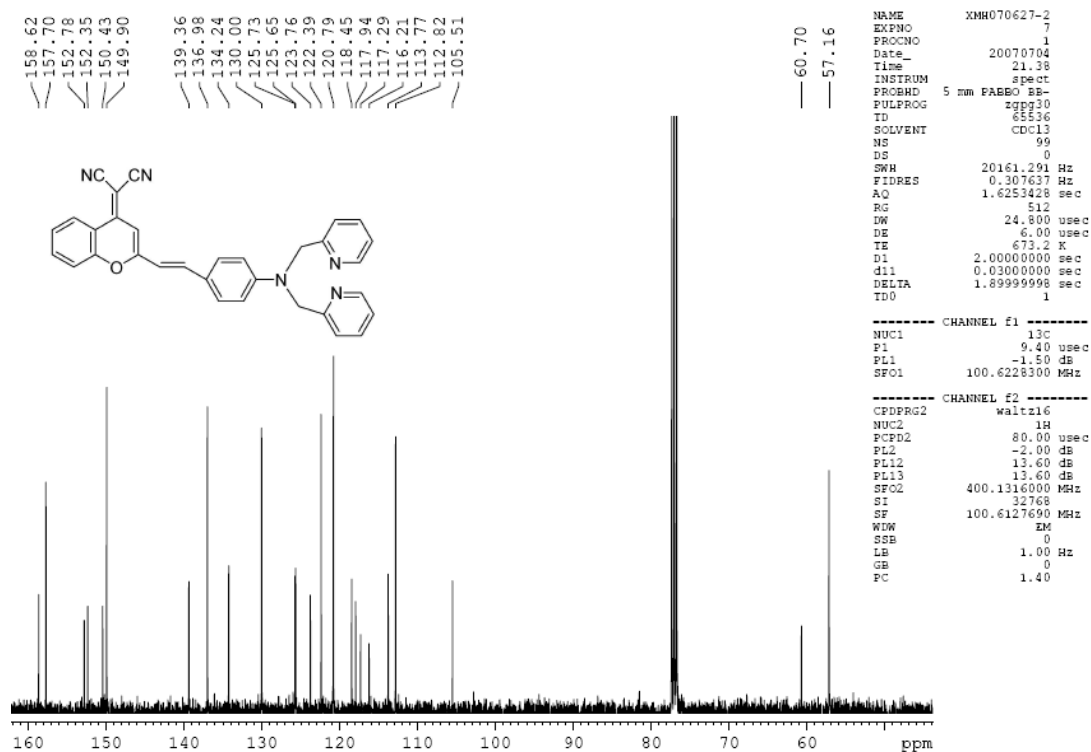


Figure S13. ¹³C- NMR of DCCP in CDCl₃ (100 MHz).

Elemental Composition Report

Page 1

Multiple Mass Analysis: 4 mass(es) processed

Tolerance = 5.0 mDa / DBE: min = -20.0, max = 100.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

30 formula(e) evaluated with 6 results within limits (up to 50 closest results for each mass)

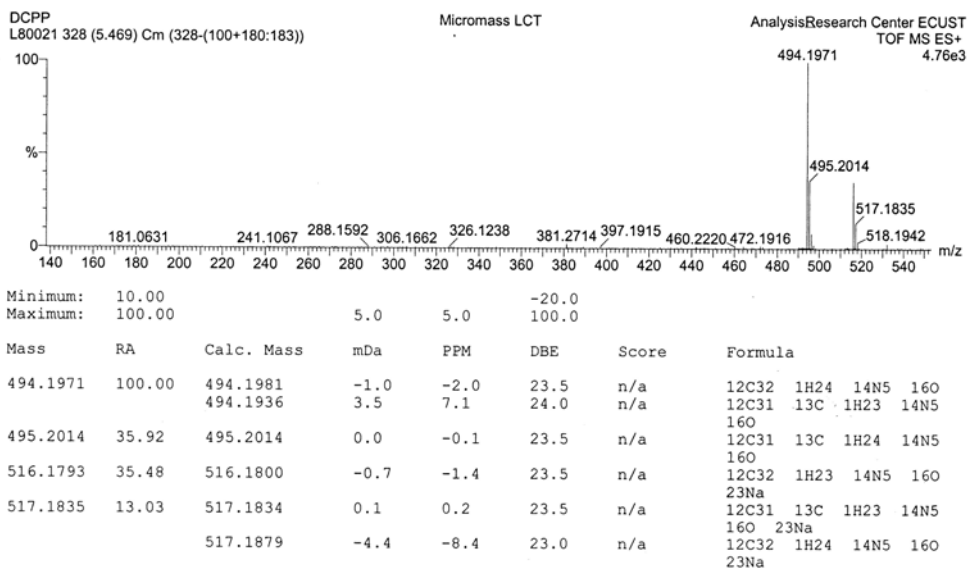


Figure S14. HRMS spectra of DCCP.