Electronic Supplementary Information (ESI)

New colorimetric fluorescent sensor for ratiometric detection of cyanide in solution, paper strips, and in cells

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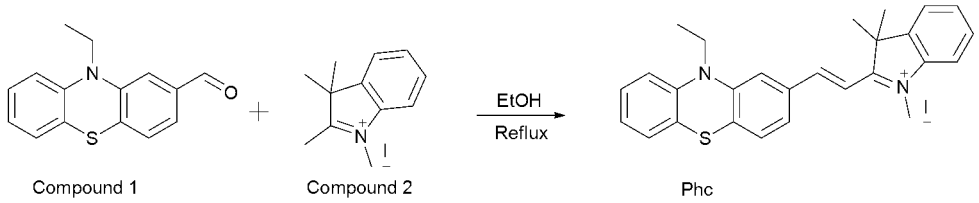
CONTENTS

1. Synthesis of Probe Phc.



Compound 1 Compound 2 Phc

Compound 1 was prepared according the reported procedure.[S1] Compound 2 was purchased from Sigma-Aldrich. For the preparation of **Phc compound**, compound 1 (0.255 g, 1.0 mmol) and compound 2 (0.301 g, 1.0 mmol) were dissolved in 20 ml ethanol. The reaction mixture was refluxed with stirring for 12 h and then evapor

At0ed in vacuum. The residue was purified by column chromatography on silica gel (CH_2Cl_2 / ethanol, 10:1 v/v) to give Phc (0.197 g) as a dark blue solid.[S2] Yield, 48%. ^{1}H NMR (600MHz, $CDCl_3$) δ 8.5(m, 1H), 8.1(d, 1H), 7.5(m, 5H), 7.2(d, 1H), 7.1(d, 1H), 7.0(m, 3H), 4.4(s, 3H), 4.0(q, 2H), 1.8(s, 6H), 1.5(t, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 181.03，153.36，150.25，142.62，141.94，141.55，129.57，129.52，129.16，128.10，127.72，127.31，123.96; HRMS (positive mode, m/z): Calcd. 255.0718, found 255.0725 for $[M + H]^+$.

The Phc-CN compound could be conveniently synthesized via the condensation of Phc and 2 equiv. of $(CH_3CH_2CH_2CH_2)_4N(CN)$ in ethanol at room temperature (yield: 95%), and purified by column chromatography on silica gel (CH_2Cl_2) as a pale green color. Note: the product is very unstable, and will decompose when exposed in the air. ^{1}H NMR (600MHz, $CDCl_3$) δ 7.3 (s, 3H), 7.2 (m, 1H), 7.2 (d, 1H), 7.1 (dd 1H), 7.1 (d, 1H), 7.0 (m, 1H), 6.9 (m, 3H), 6.6 (d, 1H), 6.1 (d, 1H) 4.0 (q, 2H), 2.8 (s, 3H), 1.6 (d, 6H), 1.5 (t, 3H); ^{13}C NMR (150 MHz, CDCl3) δ 148.62，145.30，144.35，136.60，134.88，128.29，127.42，127.40，126.70，125.00，122.64，120.28，115.13，114.93，108.84，80.47，49.14，45.85，41.96，31.58，24.51，23.01，12.94; HRMS (positive mode, m/z): Calcd. 437.1926, found 438.1935 for $[M + H]^+$.

References

[S1] WANG Wei, ZHANG Ying-mu, LI Yao-xian, ZHAO Qing, Chem. Res. Chin. Univ. 2013, 29 (4) , 632–637.

[S2] Xin Lv, Jing Liu, Yunlong Liu, Yun Zhao, Yuan-Qiang Sun, Pi Wang and Wei Guo,

Chem. Commun., 2011, 47, 12843–12845.

2. Characterization of the compounds.

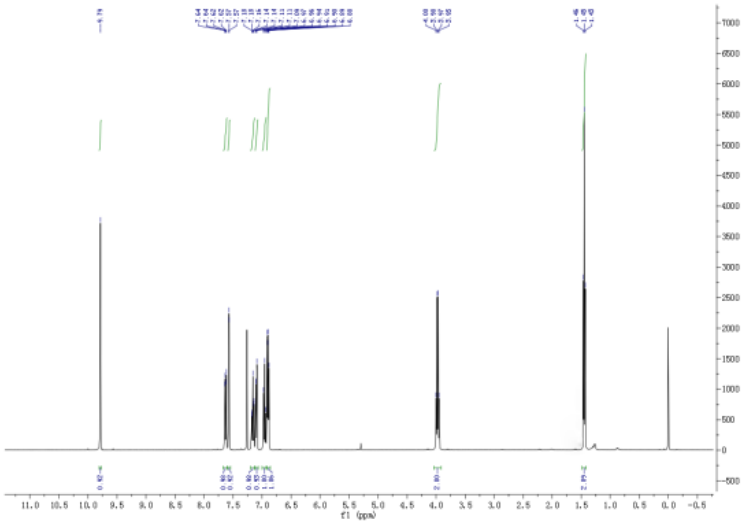
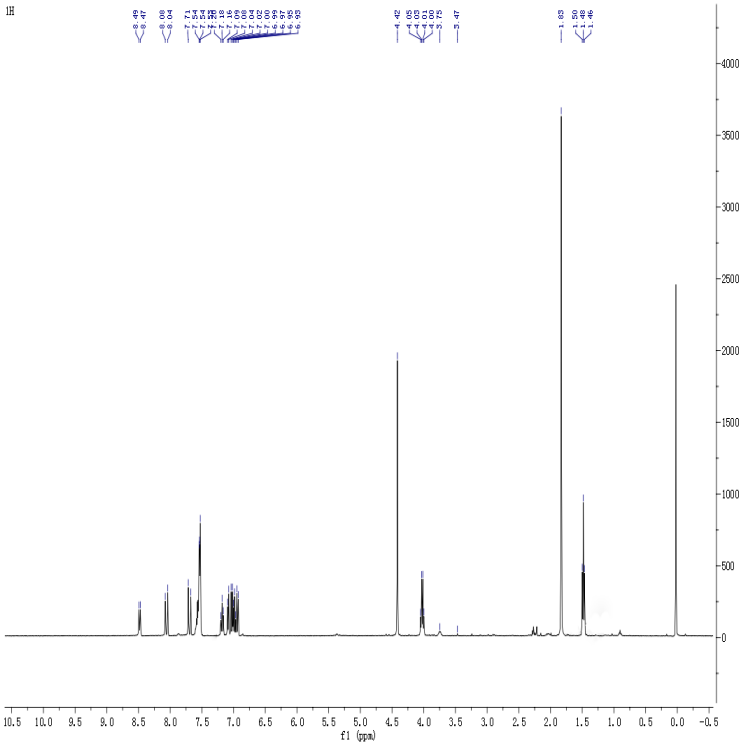


Fig. S1 ^{1}H NMR spectrum of Compound 1 in $CDCl_3$.



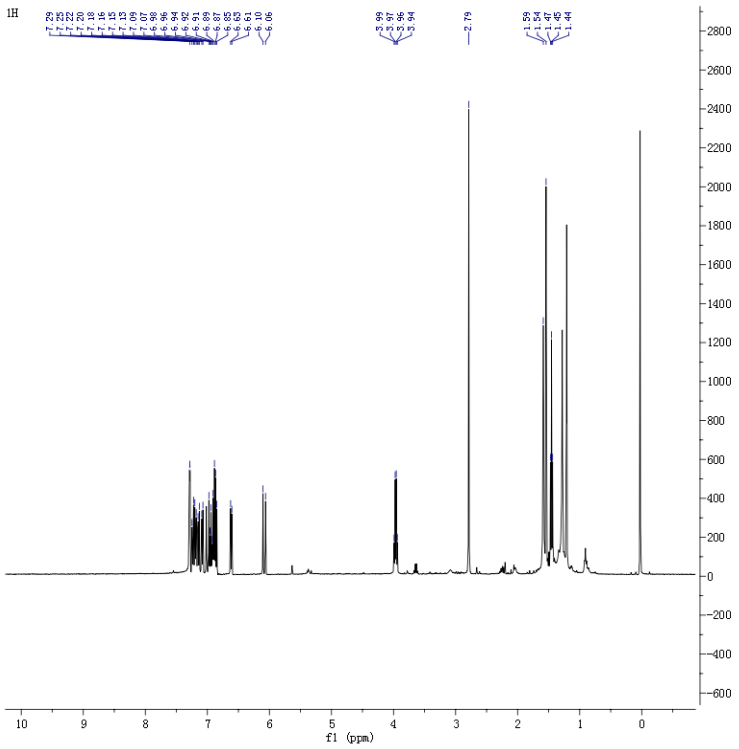
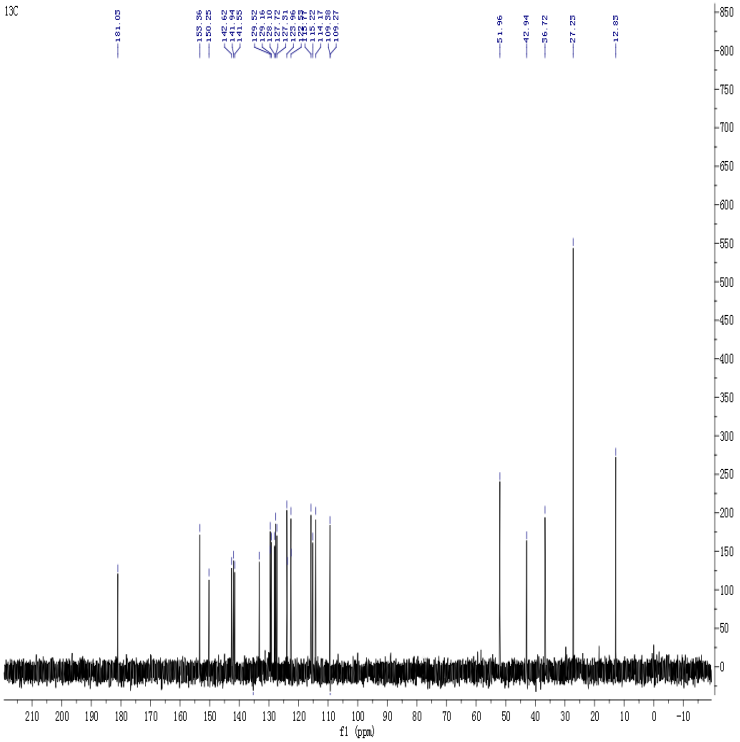


Fig. S2 ^{1}H NMR charts of Phc in $CDCl_3$ (top) and Phc-CN^- in $CDCl_3$ (below), respectively.



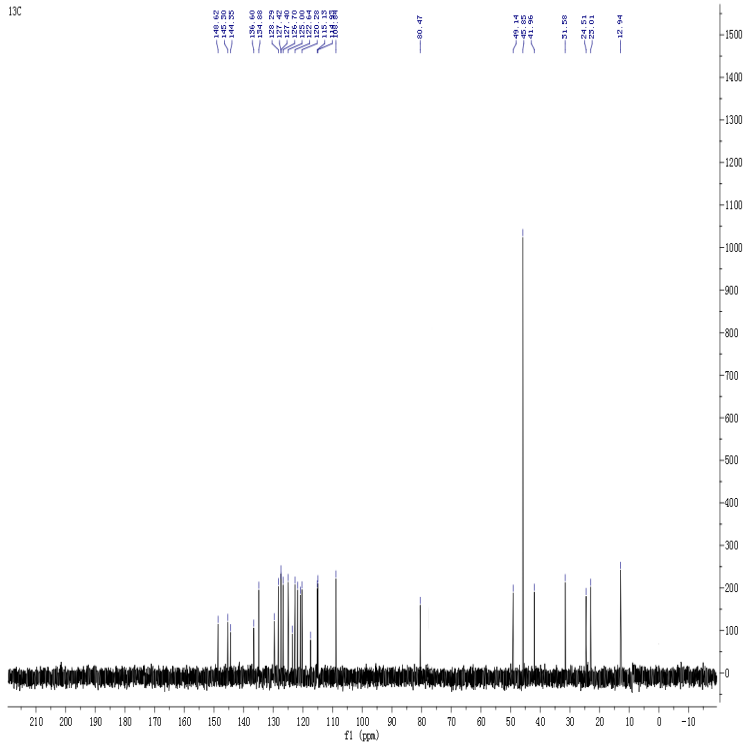


Fig. S3 ^{13}C NMR charts of Phc in $CDCl_3$ (top) and Phc-CN^- in $CDCl_3$ (below), respectively.

3. Supplemental spectra

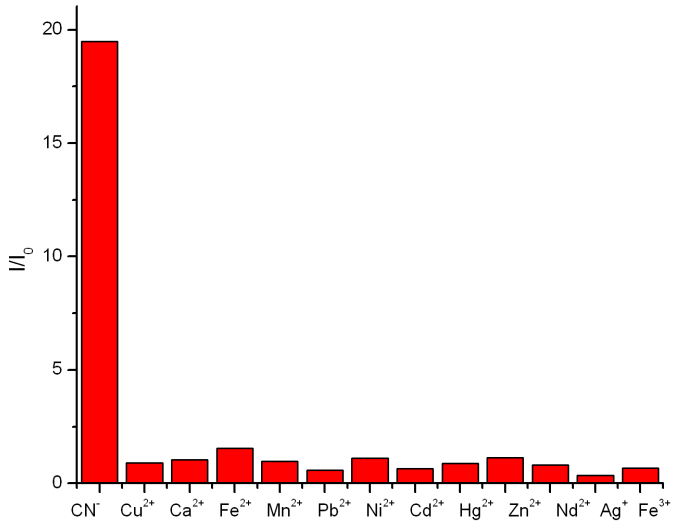


Fig. S4 Variation of the relative fluorescence intensity at 488 nm of Phc (10.0 μM) in the presence of CN^- (35.0 μM) and metal cations ($Cu^{2+}(Cu(ClO_4)_2)$ / $Zn^{2+}(Zn(ClO_4)_2)$/$Ca^{2+}(Ca(ClO_4)_2)$/$Fe^{2+}(Fe(ClO_4)_2)$/$Ni^{2+}(Ni(ClO_4)_2)$/$Mn^{2+}(Mn(ClO_4)_2)$/$Pb^{2+}(Pb(ClO_4)_2)$/$Cd^{2+}(Cd(ClO_4)_2)$ /$Hg^{2+}(Hg(ClO_4)_2)$/$Nd^{2+}(Nd(ClO_4)_2)$/$Ag^{+}(AgClO_4)$/$Fe^{3+}(Fe(ClO_4)_3)$, the concentration of each metal cations was 350 μM; all solutions were excited at 350 nm, Slits: 5 nm/ 5 nm.

Fig. S5 From left to right (A-H) are photographs under fluorescence and visible light of Phc(10μM) with the addition of CN^- (0-3.5 eqiv.;0 eqiv., 0.5 eqiv., 1 eqiv., 1.5 eqiv., 2 eqiv., 2.5 eqiv., 3 eqiv., 3.5 eqiv.).

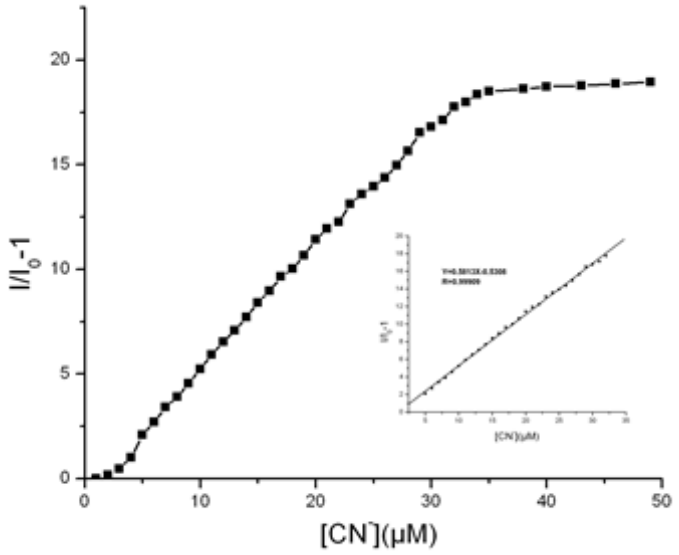


Fig. S6 I/I_0-1 intensity vs. $[CN^-]$ plot with corresponding liner fit analysis data.

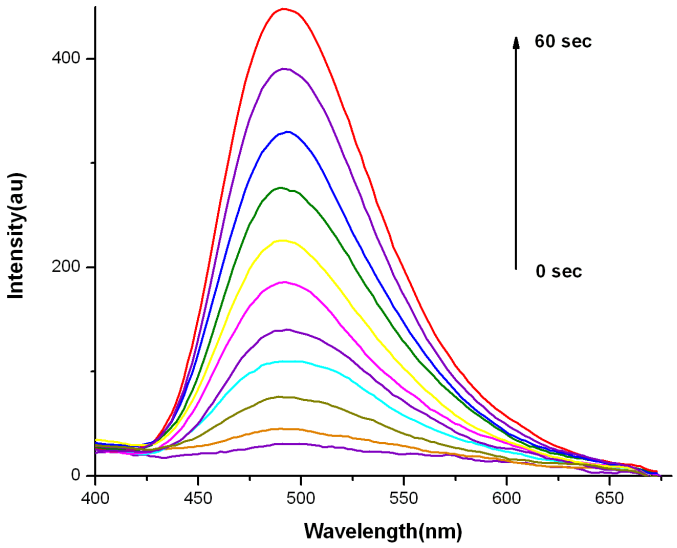
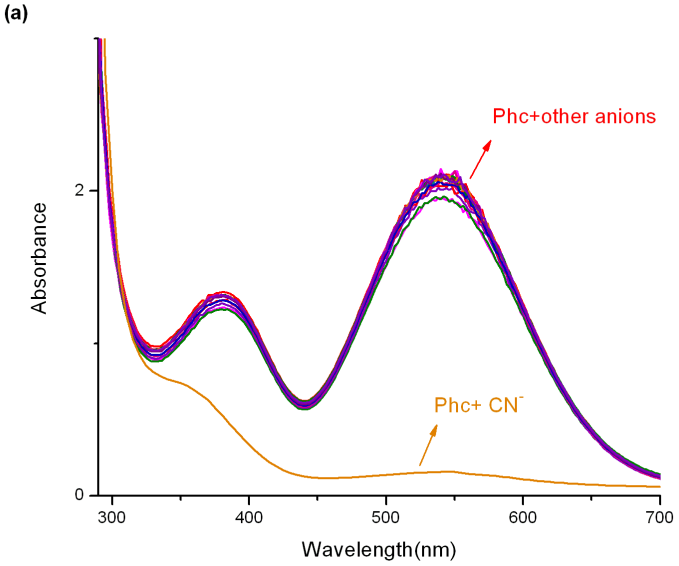


Fig. S7 Time-dependent fluorescence changing of Phc (10 μM).



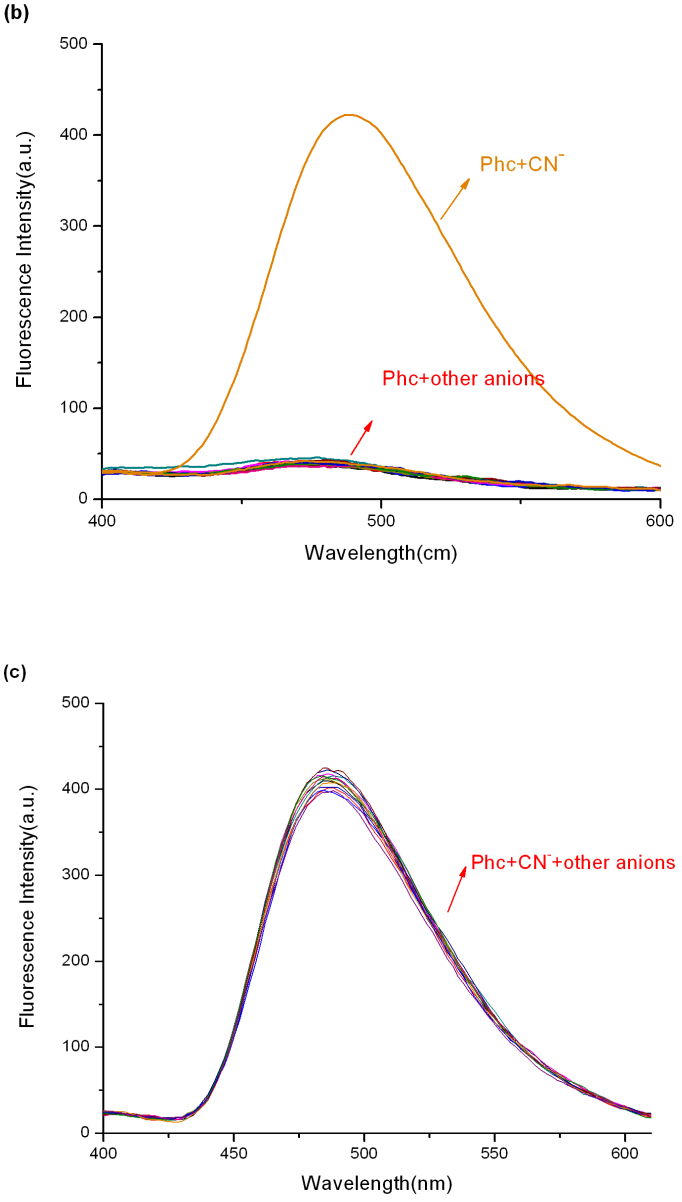


Fig. S8 (a) Absorption spectra of Phc (100 μM) and (b) fluorescence spectra of Phc (10 μM) in the presence of anions (35 equiv.); (c) Fluorescence spectra of Phc (10 μM) with CN^- (3.5 equiv.) in the addition of other anions (CN^-, F^-, Cl^-, Br^-, I^-, N_3^-, SCN^-, NO_3^-, EDTA, CH_3COO^-, $H_2PO_4^-$, HSO_3^- HPO_4^{2-}, SO_4^{2-}).

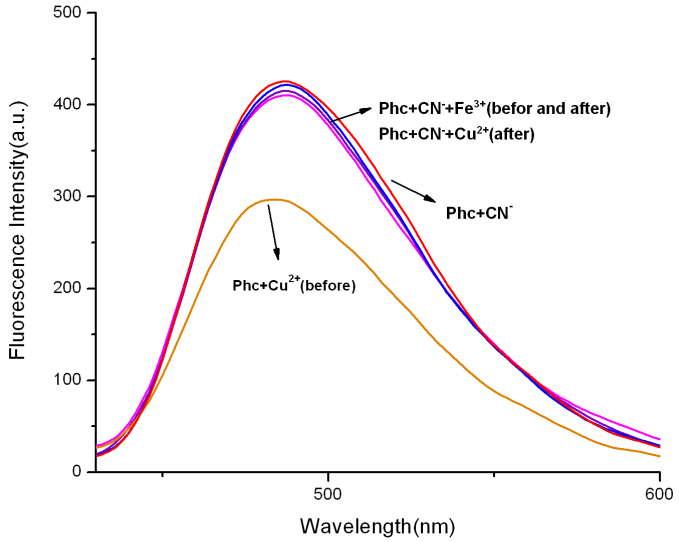


Fig. S9 Fluorescence spectra of Phc (10 μM) with CN^- (3.5equiv.) in the presence of Fe^{3+} and Cu^{2+}.

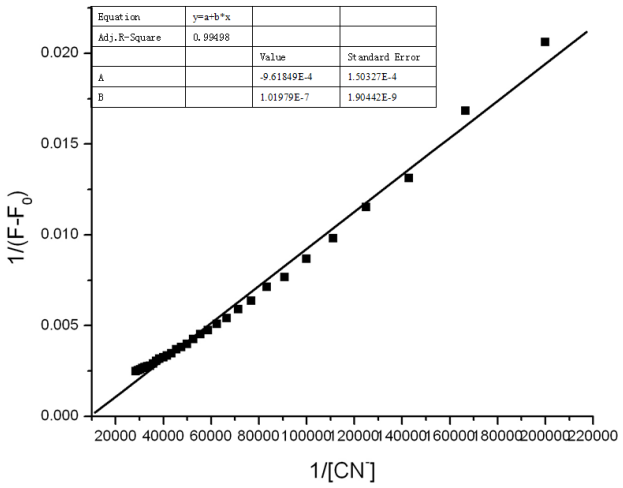


Fig. S10 Benesi-Hildebr plot from emission titration data of Phc (10μM) with CN^-.

The Benesi-Hildebrand equation: $1/(F\text{-}Fo) = 1/\{Ka(F_{max}–F_0)\ [CN^-]_n\}+1/[F_{max}\text{-}Fo]$

Here F_0 is the fluorescence of the sensor in the absence of CN^-, F is the fluorescence recorded in the presence of added guest, F_{max} is the fluorescence in presence of added $[CN^-]_{max}$, Ka is the association constant.