Supplementary Information (SI)

For

A Highly Sensitive "ON-OFF" Optical Sensor for the Selective Detection of Cyanide Ions in 100% aqueous solutions Based on Hydrogen Bonding and Water Assisted Aggregation Induced Emission

Ramo Nazarian, Hossein Reza Darabi,† Kioumars Aghapoor, Rohoullah Firouzi and Hani Sayahi

Nano & Organic Synthesis Lab., Chemistry & Chemical Engineering Research Center of Iran, Pajoohesh Blvd., km 17, Karaj Hwy, Tehran 14968-13151, Iran. Tel.: +98 21 44787720; Fax: +98 21 44787762

darabi@ccerci.ac.ir; r darabi@yahoo.com

Table of contents

<u>Page</u>

Scheme S1.Thesynthesis and experimental section of 14
Table S1.The quantum yield calculation7
Fig.S1. ¹ HNMRof 1 and its expantion spectrum8
Fig.S2. ¹³ C NMR (125 MHz, DMSO- <i>d</i> ₆) spectrum of 18
Fig.S3.Mass spectrum of 19
Fig.S4.IR spectra of 19
Fig.S5. HPLC of 110
Fig.S6.The effect of pH on the fluorescence of 1 with and without CN ⁻ ions in aq. buffer solution
Fig.S7. pH dependence of 1 on CN ⁻ measured by UV-vis experiment11
Fig.S8. Competition of CN ⁻ (1 eqiv.) with various an ions (10 eqiv.) under UV-vis measurement.
Fig.S9. Photographs of CN^{-} ion with other competing ions by naked eye under 365 nm UV light
Fig.S10.Competition of CN ⁻ (1eqiv.) with various metal ions(10eqiv.)under UV-vis measurement
Fig.S11. UV-vis spectra of 1 (0.1 μ M) upon addition of extracted cyanide-containing solution
from apricot, peach and bitter almond solutions (0.3 µM)13
Fig.S12. UV-vis spectra of 1 (0.1 μ M) in DMF, upon increasing volume percentages of water
from 0% to 58%14
Fig.S13. ¹ H NMR titration of 1 under addition of water (A) and then CN ⁻ ions (B) in DMSO- <i>d6</i> 14
Fig.S14. ¹³ CNMR titration of 1 with CN ⁻ ions in DMSO- <i>d6</i> 15

Fig.S15. Morphology of 1 before (left) and after (right) the addition of CN ⁻ measured by SEM
Fig.S16. Morphology of 1 before (left) and after (right) the addition of CN ⁻ measured by TEM
Fig.S17. Dynamic light scattering measurements of 1in the absence (up) and presence (down) of
1 eq. of cyanide in water17
Fig.S18. Self-assembly behavior of 1 : (left) in H ₂ O ; (Right) in DMF18
Fig.S19. The UV–vis spectral changes of 1 (1 equivalent) after the sequential addition of CN^-
and HCl solutions. The time after each addition of HCl is 30 seconds18
Scheme S2. Proposed optical sensing mechanism of 119
Table S2. Comparison with other AIEgen probes
References





Experimental

Materials and instrumentation

All chemical reagents and solvents were of analytical grade and commercially available. The fluorescence spectra were carried out on a Jasco FP-6500 spectrofluorimeter. The absorbance spectra were recorded on an Agilent 8453 UV-Vis spectrophotometer. Mass spectra were obtained on a Fisons instrument. ¹H NMR was measured by Varian 500MHz. Infrared spectra were recorded on a Perkin Elmer 883 spectrometer. Surface morphology of the powdered microcapsules was observed using a scanning electron microscope (SEM, Tescan, Prague, Czech Republic) with the particles mounted on the stubs and sprayed with gold. Particle size distribution analysis was measured by dynamic light scattering (DLS) experiments using a Malvern Zetasizer Nano ZS instrument. TEM Images were acquired using an transmission electron microscope Zeiss-EM10C-100 KV. The diluted solution was dropped onto carbon-coated copper grids and then dried at environmental conditions.

Synthesis of N,N'-(pyridine-2,6-diyl)bis(2-(2,4-dichlorophenoxy)acetamide) 1.

A solution of 2,6-diaminopyridine (109 mg, 1 mmol) and 2-(2,4-dichlorophenoxy)acetic acid (442 mg, 2 mmol) in MeOH (15 mL) was refluxed for 3h. After cooling down to room

temperature, the solvent was evaporated and the crude product was recrystallized from water to afford the green needle solid in 80% yield.

Compound 1: $C_{21}H_{15}O_4N_3Cl_4$, m.p. 140 °C (decomposed), IR (KBr, cm-1): 3444 (N-H stretch), 1721 (C=O), 1649 (NH bend), 1483 (C=C), 1222 (C-N); ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.55 (d, *J* = 2.6 Hz, 2H), 7.35 – 7.30 (m, 2.6, 8.9 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.9 Hz, 2H), 5.74 (d, *J* = 8.0 Hz, 2H), 4.72 (s, 4H); ¹³C NMR (125 MHz, DMSO-*d*₆) δ 170.98, 155.60, 153.11, 142.47, 129.72, 128.31, 124.90, 122.59, 115.35, 95.38, 66.37.; MS (EI), m/z (rel. intensity %) 515 (M⁺, 10%), 220 (61%, dichlorophenoxy acetamide moeity), 162 (100%, dichlorophenol moeity), 109 (80%, diaminopyridine moeity).

Fluorescence and UV-vis titration measurements of 1 with NaCN

Caution: Cyanide solutions are also very toxic! The addition of cyanide in solutions of low pH can produce the very toxic cyanhydric acid gas! All the experiments are strongly recommended to do with personal protective equipment and respiratory protection under good fume hood. Generously keep any remaining residue in alkaline solution of ferrous sulfate in dedicated container (to maintain pH at 9 or higher).

Receptor **1** (5.15 mg, 0.01 mmol) was dissolved in 100 mL buffer solution pH 7.4 of water to make the final concentration of 0.1 mM. NaCN (2.45 mg, 0.05 mmol) was dissolved in 100 mL buffer solution pH 7.4 of water. 0–400 μ L of the NaCN solution (0.5 mM) was transferred to the receptor **1** solution (0.1 mM) prepared above. After mixing them, Fluorescence and UV-vis spectra were immediately taken at room temperature.

Determination of the detection limit

To determine the signal-to-noise ratio (S/N), the absorbance and emission intensities of **1** in the presence of 1 equiv. of NaCN were measured 5 times and the standard deviation of the blank measurements was determined. The measurement of the absorbance was performed in the presence of NaCN ions, and the mean intensity was plotted as a concentration of NaCN to determine the slope. The detection limit (DL) was calculated using the following equation:

 $DL = 3\sigma/m$

where σ is the standard deviation of the intensity of **1** in the presence of 1 equiv of NaCN and *m* is the slope between the intensity (A₀/A) or (I₀/I) and concentration (C_t).

¹H NMR titrations of 1 with NaCN

Compound 1 (0.02 mmol) was added to NMR tube and then dissolved in DMSO-d6. Therefore, 0.5 and 1 equivalents of NaCN were added to 1 and after shaking the mixture for 2 minutes, the ¹H NMR spectra of each sample was taken.

The extraction of cyanide-containing solutions of bitter seeds

The well pulverized pieces of bitter seeds (4 g of each) were sonicated and stirred in 100 mL MeOH for 1h. The filtrated MeOH solutions were evaporated. The residue was dissolved in 25 mL water. The obtained cyanide-containing solutions of bitter seeds were then detected by optical methods in buffer solutions pH 5.5 and 7.4 with similar data.

Theoretical calculation

To identify stable structures of **1**, an extensive conformational search with frequency calculations was performed by some hybrid density functionals (B3LYP, CAM-B3LYP, and PBE1PBE) together with 6-31G(d) basis set. All conformers found at the above levels were reoptimized by the larger basis set 6-311++G(d,p) with three DFT methods, and then the nature of minima for the optimized structures were validated by performing harmonic vibrational calculations at the same level of theory.

Table S1. The quantum yield calculation

Sample	Α	Ι	n	φ
phenanthrene in DMF	0.059	19.4193	1.359	0.125
Compound 1 in DMF	0.0424	104.066	1.427	0.015
phenanthrene in DMF – H_2O	0.074	19.6963	1.36	0.125
Compound 1 in DMF – H_2O	1.0461	337.885	1.36	0.1

$$\frac{\phi_F}{\phi_s} = \frac{I_s}{I_F} \times \frac{A_F}{A_s} \times \frac{n_s^2}{n_F^2}$$

 $\phi_{\rm F}$ = quantum yield, I = area under the corrected emission curve, A = absorbance density of the compound at the excitation wavelength (330 nm) and n = refractive index. Subscripts s and F refer to the standard (phenanthrene) and to compound 1, respectively.



Fig.S1. ¹H NMR of 1 and its expantion spectrum



Fig.S2. ¹³C NMR (125 MHz, DMSO-*d*₆) spectrum of 1



Fig.S3. Mass spectrum of 1



Fig.S4. IR spectra of 1

Acquisition

System: ACME 9000 (97-11-17) Injection: 50 µl Mobile Phase: MeOH : ACN(85 : 15) Flow: Isocratic, 1.000 ml/min, 20:80:0 Column: Nova-pak C18 4 um 30 * 0.39 Temperature: Ambient Detector: 330 nm



Fig.S5. HPLC of 1



Fig.S6.The effect of pH on the fluorescence of 1 with and without CN⁻ ions in aq. Buffer solution



Fig.S7. pH dependence of 1 on CN⁻ measured by UV-vis experiment



Fig.S8. Competition of CN⁻(1 eqiv.) with various an ions (10 eqiv.) under UV-vis measurement.



Fig.S9. Photographs of CN⁻ ion with other competing ions by naked eye under 365 nm UV light



Fig.S10. Competition of CN⁻(1 eqiv.) with various metal ions (10 eqiv.) under UV-vis measurement.



Fig.S11. UV-vis spectra of 1 (0.1 μ M) upon addition of extracted cyanide-containing solution from apricot, peach and bitter almond solutions (0.3 μ M)



Fig.S12. UV-vis spectra of 1 (0.1 $\mu M)$ in DMF, upon increasing volume percentages of water from 0% to 58%



Fig.S13. ¹H NMR titration of 1 under addition of water (A) and then CN⁻ ions (B) to DMSO-*d6*



Fig.S14. ¹³C NMR titration of 1(A) with CN⁻ ions (B) in DMSO-d6



Fig.S15. Morphology of 1 before (left) and after (right) the addition of CN⁻ in H₂O measured by SEM



Fig.S16. Morphology of 1 before (left) and after (right) the addition of CN⁻ measured by TEM



Fig. S17. Dynamic light scattering measurements of 1in the absence (up) and presence (down) of 1 eq. of cyanide in water



Fig.S18. Self-assembly behavior of 1: (left) in H₂O; (Right) in DMF



Fig.S19. The UV–vis spectral changes of 1 (1 equivalent) after the sequential addition of CN⁻ and HCl solutions. The time after each addition of HCl in 30 seconds



Scheme S2. Proposed optical sensing mechanism of 1

Sensor	Mechanism	Sensing	Solvent	LOD	Ref.
			(response time)		
O _C NH CF ₃	Turn-on	nucleophilic addition	Water (fast)	7.74 µM	[1]
H ₃ C H ₃ C T N CH ₃	Turn-on	nucleophilic addition	Water (-)	91 nM	[2]
	Turn-off	nucleophilic addition	DMSO – Water (100 sec)	0.2 μM	[3]
	Turn-off	nucleophilic addition	DMSO – H ₂ O	0.29 µM	[4]
S-D-S-JD	Turn-on	nucleophilic addition	DMSO – H ₂ O (20 sec)	0.1 μΜ	[5]
	Turn-off	nucleophilic addition	DMSO- H ₂ O (5 min)	9.88 nM	[6]
	Turn-off	nucleophilic addition	DMF-H ₂ O	0.11 µM	[7]
je to	Turn-off	nucleophilic addition	H ₂ O	55 nM	[8]
	Turn-off	nucleophilic addition	CH3CN - H ₂ O	0.22 μM	[9]

Table S2. Comparison of 1 with other AIE based probes for detection of cyanide ions

NC T CN C C C C C C C C C C C C C C C C C C	Turn-on	nucleophilic addition	THF- H ₂ O	5.70 µM	[10]
	Turn-on	oxidative cyclization	Water	0.592 μΜ	[11]
$H_{3}C$	Turn-off	nucleophilic addition	CH3CN	-	[12]
	Color changes	Intermolecular hydrogen bonds	Glycerol	3.02 µM	[13]
	turn-on	Intermolecular hydrogen bonds	THF-H ₂ O (40 s)	0.81 µM	[14]
	turn-on & Color changes	Complex with Co	H ₂ O - MeOH	2.69 µM	[15]
pillar[5]arene	turn-on	coordinating interactions	DMF-H2O	0.0771 μM	[16]
Cho-ja, Cho-ja, Cho-ja,	turn-on	Deprotonation	DMSO	0.745 μΜ	[17]
HI ONHA	turn-off	nucleophilic addition	99% aqueous DMSO solution	67.4 nM	[18]
$\begin{array}{c} Cl \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ $	turn-off	Intramolecular hydrogen bonds	H ₂ O (5 sec)	PL (8.2 nM) and UV-vis (53 nM)	This work

References

[1] L. Peng, M. Wang, G. Zhang, D. Zhang, D. Zhu, A Fluorescence Turn-on Detection of Cyanide in Aqueous Solution Based on the Aggregation-Induced Emission, Org. Lett. 11 (2009) 1943–1946.

[2] X. Huang, X. Gu, G. Zhang, D. Zhang, A highly selective fluorescence turn-on detection of cyanide based on the aggregation of tetraphenylethylene molecules induced by chemical reaction, Chem. Commun. 48 (2012) 12195-12197.

[3] Y. Zhang, D. Li, Y. Li, J. Yu, Solvatochromic AIE luminogens as supersensitive water detectors in organic solvents and highly efficient cyanide chemosensors in water, Chem. Sci. 5 (2014) 2710–2716.

[4] W. Chen, Z. Zhang, X. Li, H. Ågren, J. Su, Highly sensitive detection of low-level water content in organic solvents and cyanide in aqueous media using novel solvatochromic AIEE fluorophores, RSC Adv. 5 (2015) 12191–12201.

[5] Y. Sun, Y. Li, X. Ma, L. Duan, A turn-on fluorescent probe for cyanide based on aggregation of terthienyl and its application for bioimaging, Sens, Actuators B. 224 (2016) 648-653.

[6] X. Yang, X. Chen, X. Lu, C. Yan, Y. Xu, X. Hang, J. Qu, R. Liu, A highly selective and sensitive fluorescent chemosensor for detection of CN^{-} , SO_3^{2-} and Fe^{3+} based on aggregation-induced emission, J. Mater. Chem. C. 4 (2016) 383–390.

[7] Y. Li, H. Zhou, W. Chen, G. Sun, L. Sun, J. Su, A simple AIE-based chemosensor for highly sensitive and selective detection of Hg^{2+} and CN^{-} , Tetrahedron. 72 (2016) 5620–5625.

[8] X. L. Lu, M. Xia, Detection of cyanide by a novel probe with a V-shaped structure based on aggregation of the probe adduct, RSC Adv. 6 (2016) 85787–85794.

[9] X. Chen, L. Wang, X. Yang, L. Tang, Y. Zhou, R. Liu, J. Qu, A new aggregation-induced emission active fluorescent probe for sensitive detection of cyanide, Sens. Actuators B. 241 (2017) 1043–1049.

[10] M.H. Chua, H. Zhou, T. T. Lin, J. Wu, J. Xu, Triphenylethylenyl-based donor–acceptor– donor molecules: Studies on structural and optical properties and AIE properties for cyanide detection, J. Mater. Chem. C. 5 (2017) 12194–12203.

[11] C. Liang, S. Jiang, Fluorescence light-up detection of cyanide in water based on cyclization reaction followed by ESIPT and AIEE, Analyst. 142 (2017) 4825–4833.

[12] K. Keshav, A. Dvivedi, M. Ravikanth, Synthesis of Dicyanovinyl SubstitutedE-Diphenyldipyrroethene and its Selective Application for Cyanide Sensing, Chem. Select. 2 (2017) 2014–2020.

[13] H. Yao, J. Wang, S. S. Song, Y. Q. Fan, X. W. Guan, Q. Zhou, T. B. Wei, Q. Lin, Y. M. Zhang, A novel supramolecular AIE gel acts as a multi-analyte sensor array, New J. Chem. 42 (2018) 18059–18065.

[14] Q. Niu, T. Sun, T. Li, Z. Guo, H. Pang, Highly sensitive and selective colorimetric/fluorescent probe with aggregation induced emission characteristics for multiple targets of copper, zinc and cyanide ions sensing and its practical application in water and food samples, Sens. Actuators B. 266 (2018) 730–743.

[15] M. T. Gabr, F. C. Pigge, A fluorescent turn-on probe for cyanide anion detection based on an AIE active cobalt(ii) complex, Dalton Trans. 47 (2018) 2079–2085.

[16] X. Q. Ma, Y. Wang, T. B. Wei, L. H. Qi, X. M. Jiang, J. D. Ding, W. B. Zhu, H. Yao, Y.M. Zhang, Q. Lin, A novel AIE chemosensor based on quinoline functionalized

23

Pillar[5]arene for highly selective and sensitive sequential detection of toxic Hg2+ and CN⁻, Dye. Pigment. 164 (2019) 279–286.

[17] Q. Lin, X. W. Guan, Y. Q. Fan, J. Wang, L. Liu, J. Liu, H. Yao, Y. M. Zhang, T. B. Wei, A tripodal supramolecular sensor to successively detect picric acid and CN⁻ through guest competitive controlled AIE, New J. Chem. 43 (2019) 2030–2036.

[18] Q. Zou, F. Tao, H. Wu, W. W. Yu, T. Li, Y. Cui, A new carbazole-based colorimetric and fluorescent sensor with aggregation induced emission for detection of cyanide anion, Dyes and Pigments. 164 (2019) 165-173.