Electronic Supplementary Material

A Fluorescent Supramolecular Gel and Its Application in Ultrasensitive Detection of CN^- by Anion-π Interactions

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Contents:

Synthesis of compound **H**.

The mixture of 1-Bromohexadecane (7.604 g, 25.0 mmol) and Potassium iodide (1.66 g, 10.0 mmol) was added to a solution of Potassium carbonate (1.38 g, 10.0 mmol) and 2-Hydroxy-1-naphthaldehyde (0.860g, 5.0 mmol) in acetone (200 mL). The mixture was heated and refluxed under nitrogen atmosphere for 72 h at 65℃. Subsequently, the crude product was filtered and the solvent was removed, solid product was recrystallized with acetonitrile and pure water. The white pure product **H** was collected by filtration, and dried under vacuum (1.3138 g, 66%). M.p.: 131-134 ℃. ^{1}H NMR ($CDCl_3$, 400 MHz) : 10.93 (s, 0H), 9.29 (d, J = 8.5 Hz, 0H), 8.04 (d, J = 9.2 Hz, 0H), 7.77 (d, J = 8.1 Hz, 0H), 7.62 (t, J = 7.1 Hz, 0H), 7.42 (t, J = 8.1 Hz, 0H), 7.28 (d, J = 9.2 Hz, 0H), 4.23 (t, J = 6.4 Hz, 0H), 1.93-1.84 (m, 0H), 1.50 (d, J = 6.0 Hz, 0H), 1.26 (s, 3H), 0.87 (d, J = 7.1 Hz, 0H).

^{1}H NMR spectrum of **H**

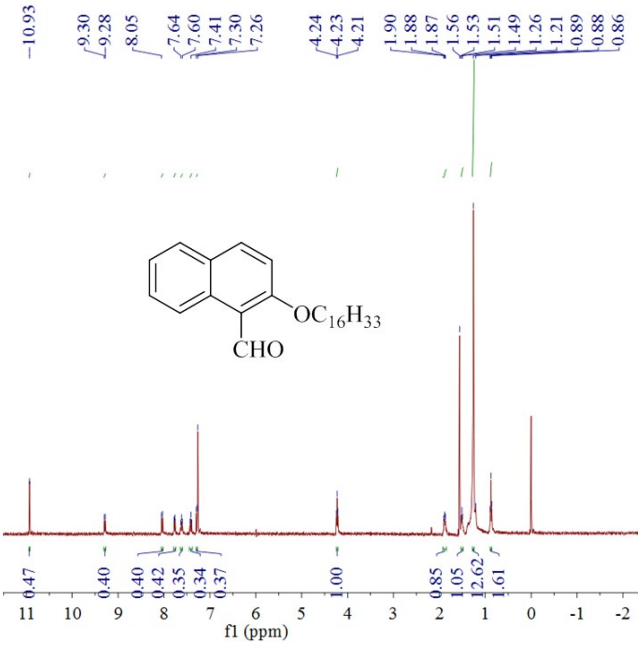


Fig. S1 ^{1}H NMR spectrum (400 MHz, 293 K) of **H** in $CDCl_3$.

ESI/MS of **H**

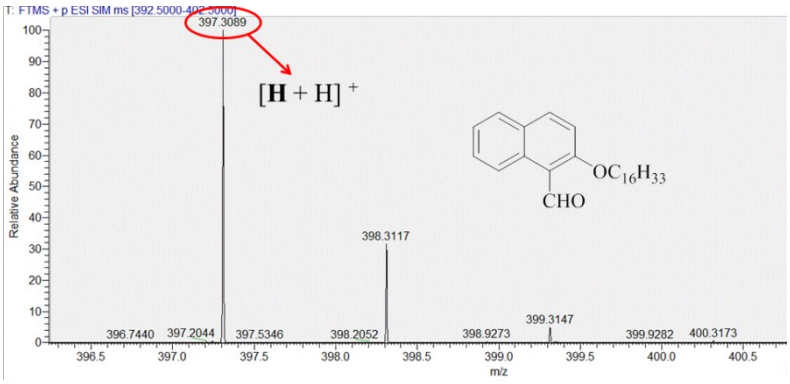


Fig. S2 The ESI-MS of **H**: [**H** + H]$^{+}$ = 397.3089.

Synthesis of compound **D**

A mixture of 1,8-naphthalenedicarboxylic anhydride (0.198 g, 1.0 mmol), and hydrazinehydrate (0.075 g, 1.5 mmol) were suspended in anhydrous ethanol (30 mL) and heated to 85 ℃ under in a 50 mL reaction flask equipped with a stir bar. After cooling to room temperature as well as adding fresh distilled water, obtained the precipitate was filtered, then with acetonitrile recrystallization get buff powder product **D** (0.178 g, Yield 84 %; m.p.: 259-263 ℃); ^{1}H NMR (DMSO-d_6, 400 MHz), δ (ppm): 8.49 (dd, J = 10.9, 1.0 Hz, 4H), 7.90-7.86 (m, 2H), 5.81 (s, 2H).

^{1}H NMR spectrum of **D**

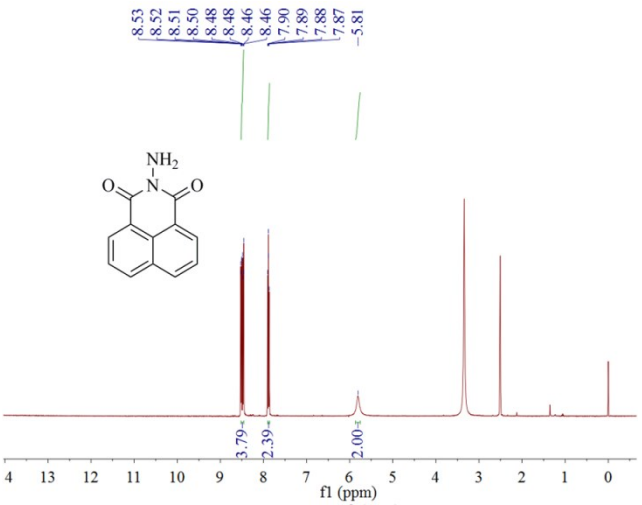


Fig. S3 ^{1}H NMR spectrum (400 MHz, 293 K) of **D** in DMSO-d_6.

ESI/MS of **D**

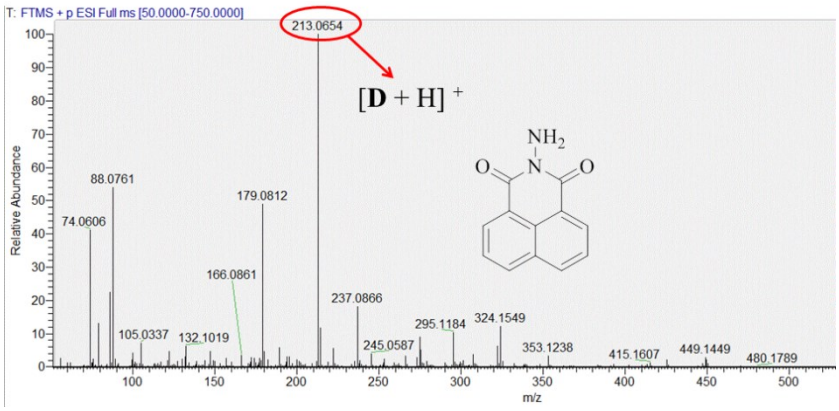


Fig. S4 The ESI-MS of **D**: $[\mathbf{D} + H]^+$ = 213.0654.

^{1}H NMR spectrum of **HD**

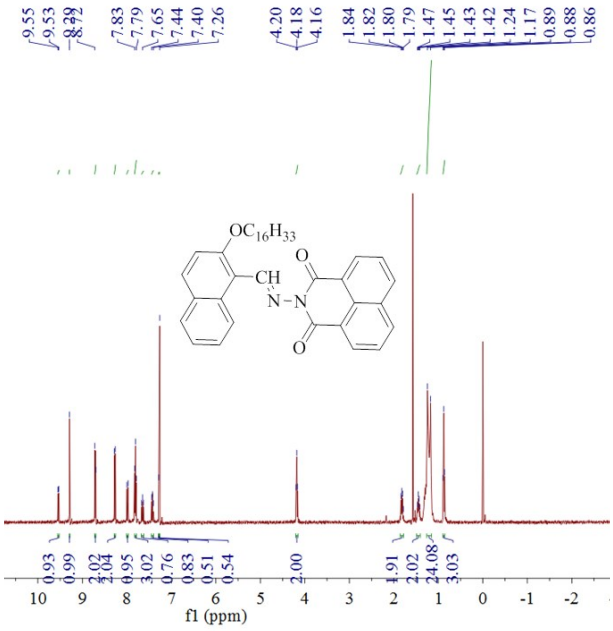


Fig. S5 ^{1}H NMR spectrum (400 MHz, 293 K) of **HD** in $CDCl_3$.

ESI/MS of **HD**

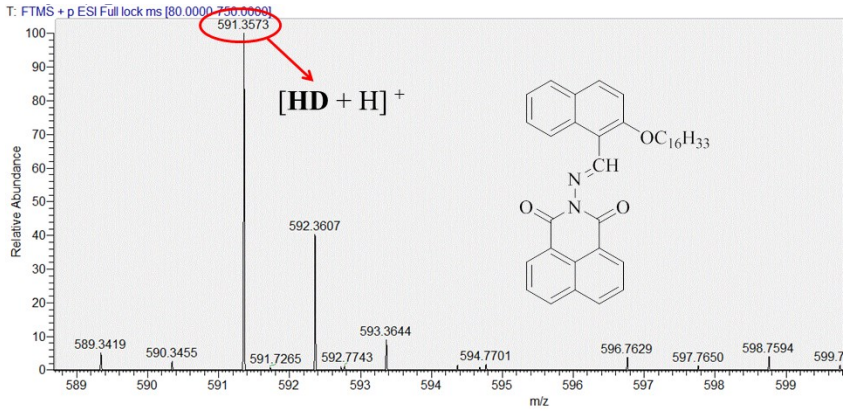
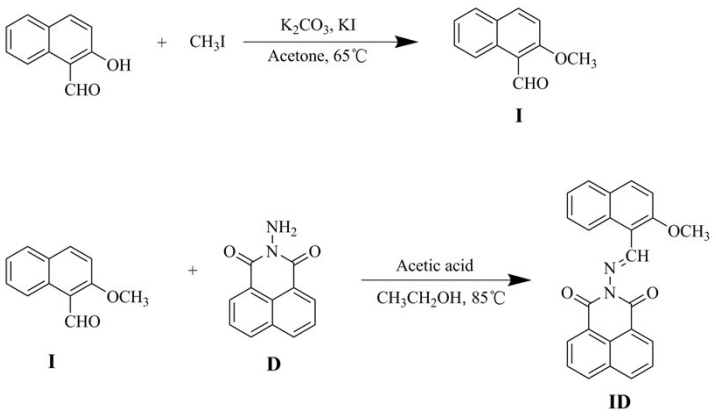


Fig. S6 The ESI-MS of **HD**: [**HD** + H]$^+$ = 591.3573.

Synthesis of compound **HI.**

The mixture of 2-methoxy-1-naphthaldehyde (2.129 g, 15.0 mmol) and Potassium iodide (1.328 g, 8.0 mmol) was added to a solution of Potassium carbonate (1.10 g, 8.0 mmol) and 2-Hydroxy-1-naphthaldehyde (0.516g, 3.0 mmol) in acetone (200 mL). The mixture was heated and refluxed under nitrogen atmosphere for 72 h at 65℃. Subsequently, Column chromatography (silica gel; petroleum ether : ethyl acetate = 20:1) afforded a white pure product **I** (0.46 g, 84%, m.p. 140-142 ◦C). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.89 (s, 1H), 9.28 (d, J = 8.7 Hz, 1H), 8.06 (d, J = 9.2 Hz, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.61 (d, J = 8.5 Hz, 1H), 7.41 (d, J = 7.0 Hz, 1H), 7.28 (s, 1H), 4.05 (s, 3H). The intermediate product (**I**) (0.186g, 1 mmol) and 2-amino-1H-benzo[de]iso-quinoline-1,3(2H)-dione (**D**) (0.2545 g, 1.2 mmol) were dispersed in 25 mL ethanol with adding acetic acid as catalyst after refluxing at 85℃ for 8 h. The resulting solution was cooled to room temperature and the white solid **ID** (0.327 mmol) in 86% yield (m.p.＞300◦C) was obtained by filtration under reduced pressure, dried in vacuum oven. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.24 (s, 1H), 8.53 (s, 4H), 8.24 (s, 2H), 7.93 (s, 2H), 7.65 (d, J = 6.9 Hz, 2H), 7.50 (s, 1H), 4.02 (s, 3H).

Synthesis of compound **ID.**



Scheme S1. Synthesis of compound **ID**.

^{1}H NMR spectrum of **I**

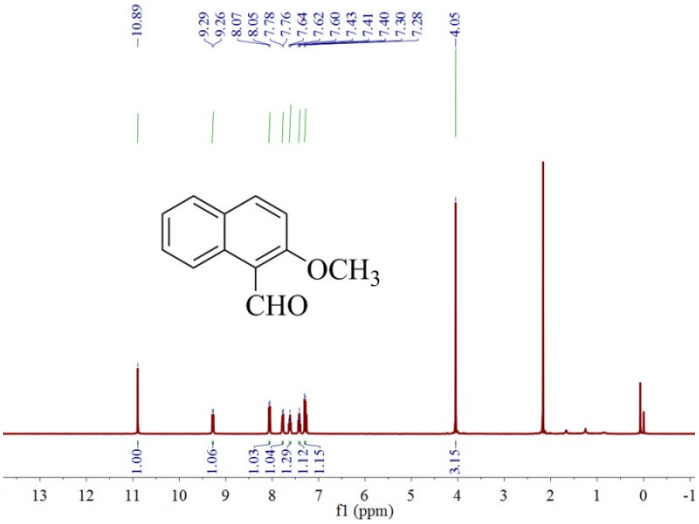


Fig. S7 ^{1}H NMR spectrum (400 MHz, 293 K) of **I** in DMSO-d_6.

ESI/MS of **I**

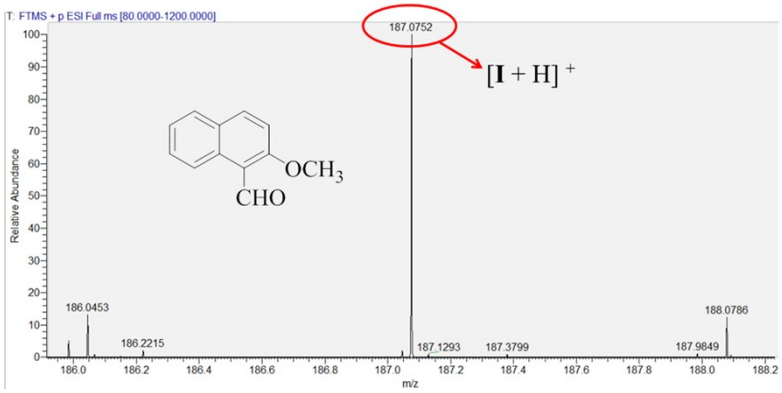


Fig. S8 The ESI-MS of **I**: $[\mathbf{I} + H]^+$ = 187.0752.

^{1}H NMR spectrum of **ID**

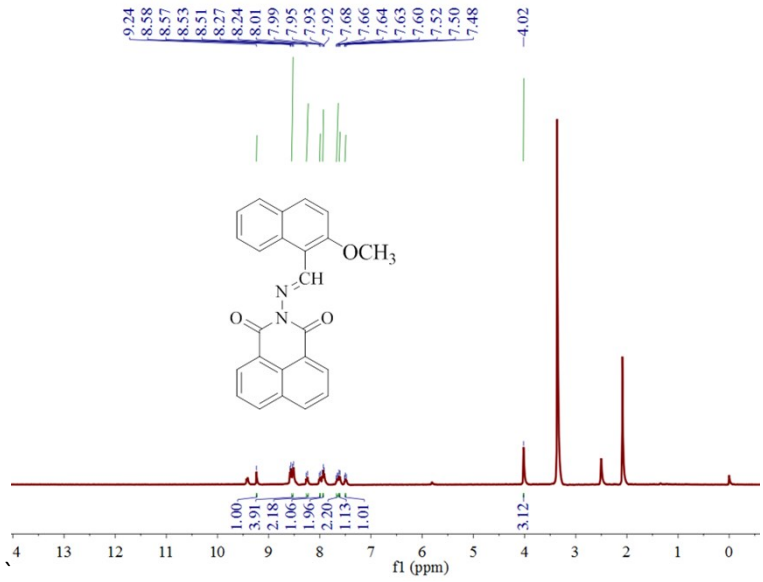


Fig. S9 ^{1}H NMR spectrum (400 MHz, 293 K) of **ID** in DMSO-d_6.

ESI/MS of **ID**

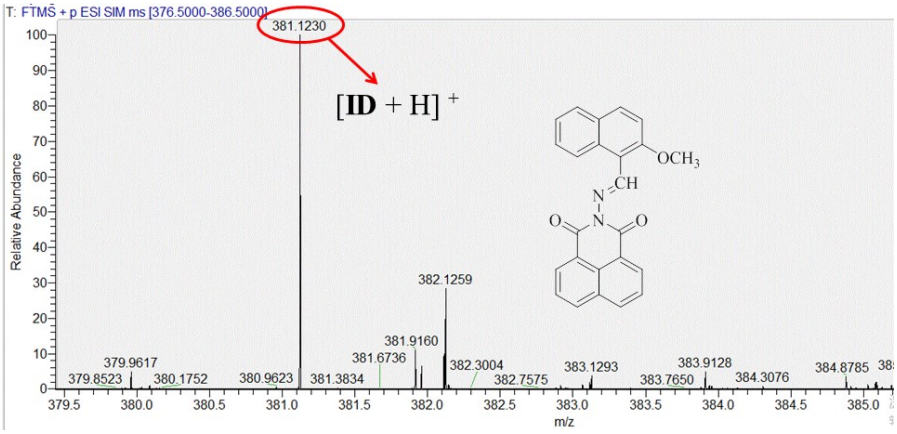


Fig. S10 The ESI-MS of **ID**: [**ID** + H]$^+$ = 381.1230.

Table S1. Gelation properties of supramolecular geltor **HD** in different solvents.

Entry	Solvent	State [a]	CGC [b] (%)	T_{gel} [c] (℃, wt%)
1	Cyclohexane	P	\	\
2	n-Hexanol	P	\	\
3	Acetone	P	\	\
4	CH_2ClCH_2Cl	S	\	\
5	CH_2Cl_2	S	\	\
6	DMSO	G	2%	70
7	DMF	G	2.5%	73
8	$CHCl_3$	S	\	\
9	Acetonitrile	P	\	\
10	Methanol	P	\	\
11	Ethanol	P	\	\
12	THF	P	\	\

[a] G, P and S denote gelation, precipitation and solution, respectively;

[b]The critical gelation concentration (wt%, 10 mg/mL = 1.0%);

[c] The gel-sol transition temperature (℃).

Selective detection studies at different equivalents of anions

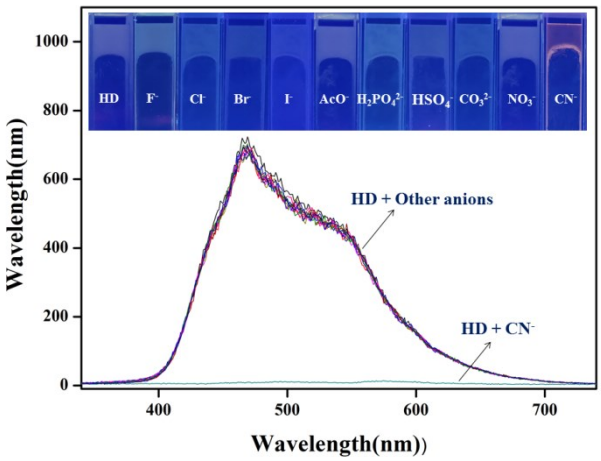


Fig. S11 Fluorescence spectra of the gel HD-G in the presence of 1 equivalents various anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, CN^-, CO_3^{2-} and NO_3^-)

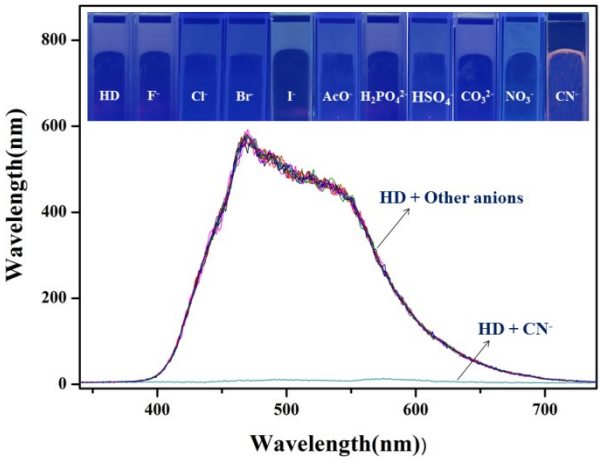


Fig. S12 Fluorescence spectra of the gel HD-G in the presence of 5 equivalents various anions (F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, CN^-, CO_3^{2-} and NO_3^-)

linear fitting for CN^-

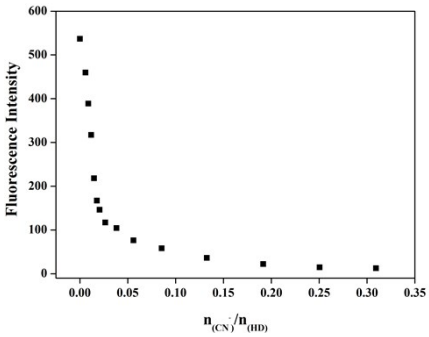


Fig. S13 The emission intensities of **HD-G** at 300 nm relying on the concentration of cyanide anion.

Determine of the fluorescent detection limit for CN^-

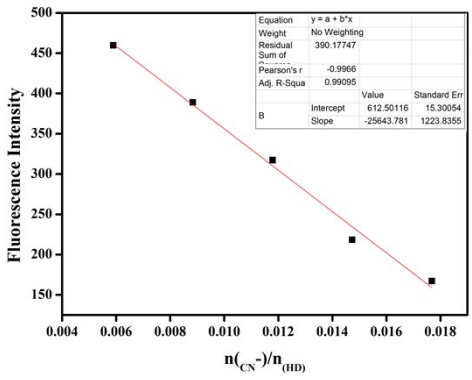


Fig. S14 The photograph of the linear range for cyanide anion.

The lowest detection limit was calculated using the following equation:

Linear Equation: Y = ‒ 25643.781 × X +612.5012 R^2 = 0.99095

S = 1230.65088 × 106 $\delta = \sqrt{\frac{\Sigma(F-\overline{F})2}{(N-1)}} =$ 1.557767 (N = 20) K = 3

LOD = K × δ/S = 1.82239 ×10^{-10} M

Calculation of the K_a

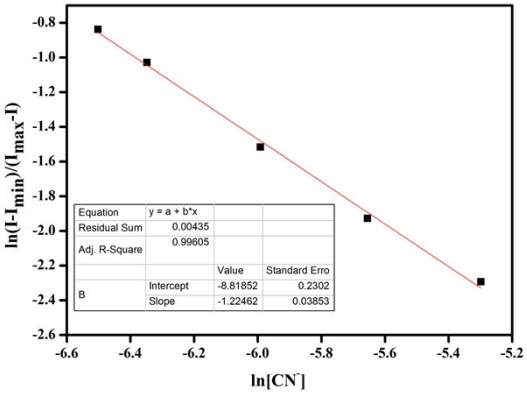


Fig. S15 The photograph of the linear fit of fluorescence titration.

$$\ln\frac{I-I_{\min}}{I_{\max}-I} = \ln K_a + \ln[G]$$

$$\ln K_a = 8.81852$$

$$\text{Slope} = -1.2$$

(The stability constant (Ka) was determined by a nonlinear least square fit of the data. I is the observed

the fluorescence intensity of **HD** at the fixed concentrations of CN^-. Imax and Imin are the corresponding maximum and minimum, respectively. G is the concentrations of CN^-.)

Partial ^1H NMR spectra of the simulant **ID** (DMSO-d_6) with various equivalents of CN^-

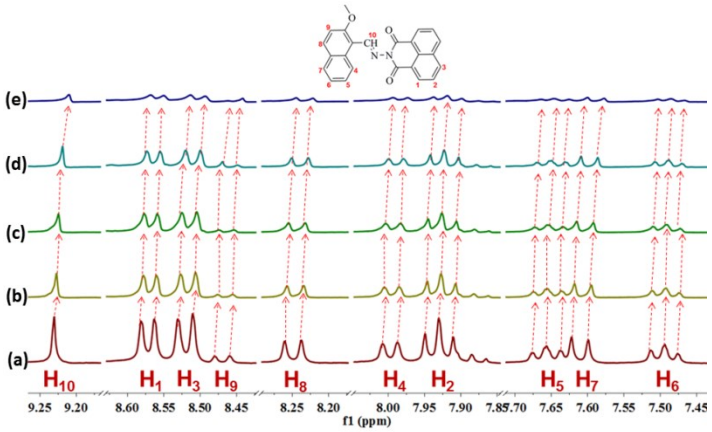


Fig. S16 Partial ^1H NMR spectra of **ID** (DMSO-d_6) with various equivalents of CN^- : (a) 0 equiv., (b) 0.1 equiv., (c) 0.2 equiv., (d) 0.5 equiv., and (e)1 equiv.

XRD of compound **HD, HD-G and HD-G**+ CN^-

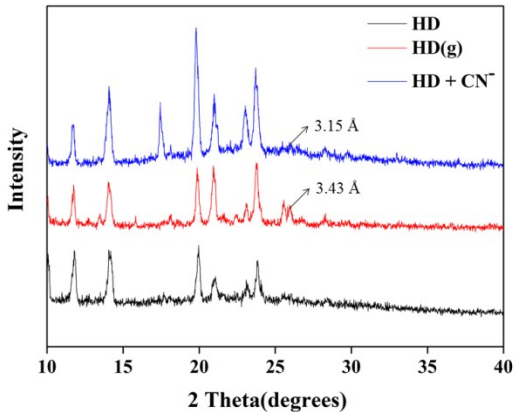


Fig. S17. Powder XRD patterns for compound of **HD**, **HD-G** xerogels and **HD-G** + CN^- xerogels.

IR spectra of compound **HD, HD-G and HD-G+** CN^-

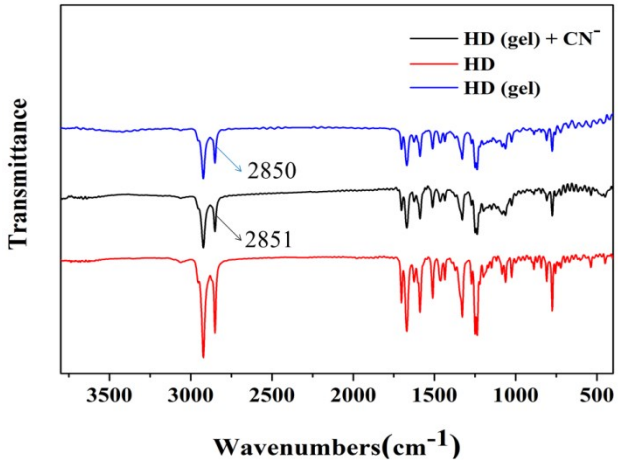


Fig. S18. FT-IR spectra of compound of **HD**, **HD-G** xerogels and **HD-G** + CN^- xerogels.

SEM micrographs of compound **HD**; the xerogel of **HD-G**; **HD-G + CN**$^-$

Fig. S19. Comparative FE-SEM micrographs of (a) the powder of compound **HD**; (b) the xerogel of **HD-G**; (c) **HD-G** + CN^- xerogels.

ESI/MS of **HD + NaCN**

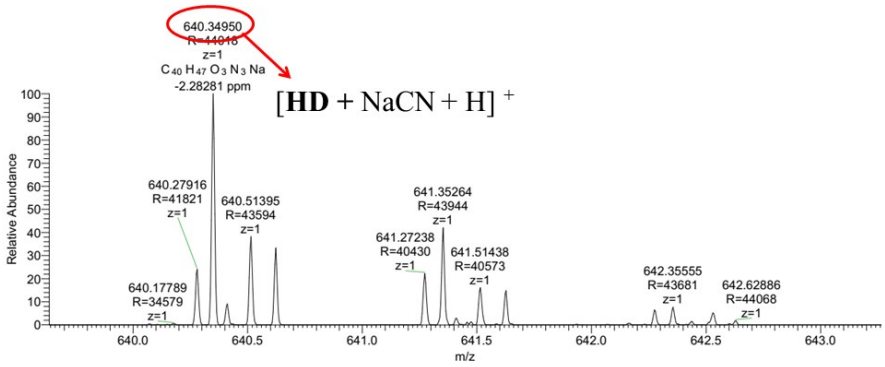


Fig. S20. The ESI/MS examined between **HD** and NaCN indicating the 1:1 stoichiometry.