Bisindole anchored mesoporous silica nanoparticles for cyanide sensing in aqueous media

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1. Instruments and reagents

All UV-vis absorption spectra were recorded on a S-3100 spectrophotometer. NMR and mass spectra were recorded on a Varian instrument (300 MHz, and 400 MHz) and JMS-700 MStation mass spectrometer, respectively. Indole, DDQ, $p$-tolualdehyde, 4-hydroxyaldehyde and all anionic compounds such as TBA$^+$ salts of F$^-$, Cl$^-$, Br$^-$, I$^-$, CH$_3$CO$_2^-$, HSO$_4^-$, H$_2$PO$_4^-$, NO$_3^-$, and CN$^-$ were purchased from Aldrich and used as received. All solvents were analytical reagents and from Duksan Pure Chemical Co., Ltd. CH$_3$CN for spectra detection was of HPLC reagent grade without fluorescent impurity. Time-of-flight Second Ion Mass Spectrometer (TOF-SIMS) was analyzed on Model PHI 7200 equipped with Cs and Ga ion guns for positive and negative ion mass detection. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2100 F instrument operated at 150 keV. IR spectra were obtained using KBr pellets, in the range 400-4000 cm$^{-1}$, with a Shimadzu FT-IR 8400S instrument, and the MS spectra were obtained with a JEOL JMS-700 mass spectrometer.

2. Detection limit of $3$ for CN$^-$

Material $3$ (10.0 μM) was dispersed in H$_2$O/CH$_3$CN (7:1, v/v) at pH 7. The constant concentration of CN$^-$ was added step-by step to the suspension of $3$ in H$_2$O/CH$_3$CN (7:1, v/v) Then, the absorbance of $3$ at 515 nm was observed at each steps. The detection limit of $3$ was calculated by reported method previously.$^{1-2}$

References
3. Supplementary spectral data

Figure S1. UV/vis spectra of 1 (20.0 μM) upon addition of various anions (30 equiv) in CH₃CN.

Figure S2. Titration profile of 1 (20.0 μM) for CN⁻ in H₂O/CH₃CN (7:1, v/v). Inset: Absorbance spectra of 1 (20.0 μM) in H₂O/CH₃CN (7:1, v/v) solution upon addition of TBA⁺CN⁻ (0, 0.1, 0.3, 0.5, 0.7, 1, 1.5, 2, 3, 10, 50, and 100 eq).
**Figure S3.** FAB-Mass spectrum of 1+CN⁻.

**Figure S4.** NMR spectra changes of 1 upon addition of CN⁻. (a) $^1$H NMR spectra of 1 only, (b) $^1$H NMR spectra of 1 and 3.0 eq of CN⁻, and (c) $^{13}$C NMR spectra of 1 and 3.0 eq of CN⁻.
Figure S5. IR spectrum of 6.

Figure S6. FT-IR spectra of (a) mesoporous silica and (b) 3.

Figure S7. TOF-SIMS spectrum of the fragment from 3, which is bisindole moiety.
Figure S8. (A) UV/vis spectra and photograph of 3 (20 μM) in the (a) absence and the presence of (b) CN⁻ (30 equiv) and (c) Cu²⁺ (30 equiv) in H₂O/CH₃CN (7:1, v/v).

Figure S9. Plot of pH values vs absorbance of 3 in the (a) absence (at 515 nm) and (b) the presence of CN⁻ (at 480 nm) in H₂O/CH₃CN (7:1, v/v).

Figure S10. Absorption spectra of 1 (black) and 1+10.0 equiv of Cu²⁺ (red) in H₂O/CH₃CN (7:1, v/v).
Figure S11. Plot of absorbance at 515 nm versus increasing quantities of CN$^-$ added to 3 suspension at pH 7 in H$_2$O/CH$_3$CN (7:1, v/v).
NMR copies

$^1$H NMR (CDCl$_3$, 400 MHz) spectrum of 4.

$^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of 4.
$^1$H NMR (CDCl$_3$, 400 MHz) spectrum of 1.

$^{13}$C NMR (CDCl$_3$, 100 MHz) spectrum of 1.
2. Experimental Section

Compounds 2 and 5 were prepared following literature procedures.\textsuperscript{S1}

\textbf{Preparation of 1:} Compound 4 (100 mg, 0.3 mmol) was dissolved in CH\textsubscript{3}CN (10 mL). DDQ (0.013 g, 0.06 mmol) solution of CH\textsubscript{3}CN was added dropwise to the solution. This reaction was allowed to stir for 5 h to give a dark red precipitate, which was filtered and washed with CH\textsubscript{3}CN. Recrystallization from ethyl ether gave 1 (30 mg) in 30% yield. IR (KBr pellet, cm\textsuperscript{-1}): 2543, 2301; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) \(\delta\) 7.84 (br s, 2H), 7.57 (d, 2H, \(J=7.6\) Hz), 7.43 (d, 2H, \(J=8.2\) Hz), 7.27 (m, 4H), 6.99 (m, 4H), 2.48 (s, 3H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\) 141.3, 136.7, 132.0, 129.5, 128.6, 125.3, 123.0, 121.8, 116.2, 21.8 ppm. FAB MS \textit{m/z} (M\textsuperscript{+}): calcd for 334.4. found 334.2.

\textbf{Preparation of 4:} To a solution of \(p\)-tolualdehyde (100 mg, 0.83 mmol) and indole (205mg, 1.74 mmol) in methanol was added KHSO\textsubscript{4} (113 mg, 1 mmol), and the mixture was stirred at room temperature for 2 h. After evaporation of the solvent, the residue was partitioned between dichloromethane and water. The organic layer was separated and washed with water and evaporated. The crude product was purified by the column chromatography (hexane: ethyl acetate=7:1, v/v) to afford 3 (0.15 g) in 54 % yield. IR (KBr pellet, cm\textsuperscript{-1}): 1652, 1632; \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) \(\delta\) 7.87 (br s, 2H), 7.37 (d, 2H, \(J=7.5\) Hz), 7.32 (d, 2H, \(J=8.4\) Hz), 7.21 (d, 2H, \(J=7.8\) Hz), 7.13 (t, 2H, \(J=8.2\) Hz), 7.06 (d, 2H, \(J=7.8\) Hz), 6.96 (t, 2H, \(J=8.0\) Hz), 6.64 (m, 2H), 5.84 (s, 1H), 2.31 (s, 3H). \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz) \(\delta\) 141.2, 136.8, 135.7, 129.1, 128.8, 127.3, 123.8, 122.1, 120.2, 120.1, 119.4, 111.3, 40.0, 31.8, 22.9, 21.3, 14.4 ppm. FAB MS \textit{m/z} (M\textsuperscript{+}): calcd for 336.4. found 337.1.

\textbf{Preparation of mesoporous silica:} Mesoporous silica was synthesized starting from the preparation of a hydrochloric acid solution of P-123 [(poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer)]. Tetraethyl orthosilicate (TEOS) was then added and the mixture was stirred at 40 °C for 20 h. The molar composition was 1:5.9:193:0.017 TEOS:HCl:H\textsubscript{2}O:P-123. The solid was aged at 65 °C for 1 day and then was filtered, washed and dried at 90 °C. To cleave the template to generate mesopores, 1.0 g of as-synthesized SBA-15 was mixed with 100 mL of 60 wt % H\textsubscript{2}SO\textsubscript{4} solution and refluxed at 95 °C for 1 day. The product was recovered by washing with water and dried at 90 °C. To generate mesopores, the acid-treated sample was heated to 200 °C in air. To remove cationic
surfactants from the resulting dried fiber-like flocculates and particles, the sample was calcined in a box furnace in air at 500 °C for 5 h, with a ramp rate of 1 °C/min.

**Preparation of the solid nanomaterial 6:** Triethoxylsilyl propyl isocyanate (100 mg) was dissolved in toluene (10 mL). Mesoporous silica nanoparticles (100 mg) were added as supporting materials. The suspension of silica was stirred under reflux conditions for 24 h in toluene. Then, the collected solid was washed copiously with toluene (50 mL) to rinse away any surplus 6 and dried under vacuum.

**Preparation of the solid nanomaterial 3:** Compound 2 (100 mg) was dissolved in toluene (10 mL). The solid material 2 (100 mg) was added as a solid. The suspension of silica was stirred under reflux conditions for 24 h in toluene. Then, the collected solid was washed copiously with toluene (50 mL) to rinse away any surplus 3 and dried under vacuum.

**Preparation of the pellet-type disk 3:** The disk-type pellets were similar to that obtained from KBr pellet. For example, the solid 3 (10 mg) was prepared as a disk-type pellet by pressure with 10,000 pound per square inch as obtained at KBr pellet. The disk-type pellets were immersed in CN⁻ (0.01 M) in H₂O/CH₃CN (7:1, v/v).

**References**