Supporting Information

A highly selective and sensitive reusable colorimetric sensor for Ag⁺ based on thiadiazole-functionalized polyacrylonitrile fiber

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1. Synthesis of DPTD

**Scheme 1.** The route for synthesis of DPTD

Compound 1 (16.7 g, 100 mmol) was dissolved in MeOH (150 mL). Concentrated H₂SO₄ (10 mL) was added and the mixture was stirred at reflux for 8 h. After cooling to room temperature, the mixture was concentrated under vacuum, diluted in H₂O (30 mL) and neutralized by the addition of solid K₂CO₃. Then the solution was extracted with EtOAc (2 × 50 mL) and the organic layers were washed with brine, dried over Na₂SO₄ and concentrated to give 2 as a white needle-like crystals, mp 117-118°C (15.6 g, 80%).¹H NMR (400 MHz, CDCl₃) δ 8.33 (d, J = 7.8 Hz, 2H), 8.04 (d, J = 7.8 Hz, 1H), 4.04 (s, 6H).

Intermediate 2 (9.75 g, 50 mmol) was dissolved in MeOH (100 mL), and then 80% hydrazine (30 mL) was added and the mixture was stirred at reflux for 4 h. After cooling to room
temperature, the mixture was concentrated under vacuum, diluted with H₂O (50 mL) and the formed precipitate was filtered. The filtrate was washed several times with distilled water to give pure 3 as a white needle-like crystal, mp 290°C (8 g, 90%). ¹H NMR (400 MHz, DMSO-d₆) δ 10.64 (s, 2H), 8.13 (m, 3H), 4.63 (s, 4H).

To a stirred solution of 3 (3.9 g, 20 mmol) in 20 mL of absolute ethanol containing potassium hydroxide (3.36 g, 60 mmol), carbon disulfide (4 g, 50 mmol) was added. The reaction mixture was stirred at room temperature for 6 h. Then the product was precipitated with ethyl ether, filtered off, washed with ethyl ether to give the corresponding potassium salt 4 in pure form as yellow powder. IR (KBr): v = 3350-3280 (NH), 1688 (C=O), 1259 (C=S) cm⁻¹.

To a stirred ice-cold concentrated sulfuric acid 10 mL, potassium salt 4 obtained above was added. The reaction mixture was left overnight and then gradually added to crushed ice. The separated precipitate was filtered off, washed with water, dried, and crystallized from ethanol to give 5 as yellowish powder, mp 288-300°C (4.2 g, 78%). ¹H NMR (400 MHz, DMSO-d₆) δ 14.92 (s, 2H), 8.27 (d, J = 7.8 Hz, 2H), 8.10 (d, J = 7.8 Hz, 1H). ¹³C-NMR (400 MHz, DMSO-d₆): δ 122.11, 140.50, 147.43 (5C, pyrid-C), 160.09, 189.57 (4C, thiadiazole ring). IR (KBr): v = 3345-3302 (NH), 1662 (C=N), 1660 (C=C), 1242 (C=S) cm⁻¹.

To a suspension of K₂CO₃ (3.32 g, 24 mmol) and KI (catalytic amount) in 30 mL of anhydrous acetone, 5 (3.11 g, 10 mmol) dissolved in 30 mL of the same solvent were added under stirring. The mixture was refluxed for 0.5 h. Methyl chloroacetate (2.39 g, 22 mmol) was dropped slowly into the stirred mixture. After 8 h, the solvent was completely evaporated in vacuum and the solid residue was washed with distilled water, collected by filtration and recrystallized from absolute ethanol to obtain the target product DPTD, m.p. 155°C (3.6 g, 79 %). ¹H NMR (400 MHz, CDCl₃) δ 8.34 (d, J = 7.8 Hz, 2H), 8.01 (d, J = 7.8 Hz, 1H) 4.24 (s, 4H), 3.83 (s, 6H). ¹³C-NMR (400 MHz, DMSO-d₆): δ 122.58, 140.55, 148.69 (5C, pyrid-C), 169.07, 168.87, 167.09 (3C, thiadiazole ring), 53.17 (2C, CH₃). IR (KBr): v = 3345-3302 (NH), 1662 (C=N), 1660 (C=C), 1242 (C=S) cm⁻¹.

2. Response time of the colorimetric fiber
3. Reusability of the colorimetric fiber

Fig. S2. Reusability of DPTD-PAN$_F$ in water after the 1st-10th (a1-a10) absorption and the 1st-10th (b1-b10) desorption in 1 × $10^{-5}$ mol/L Ag$^+$ solution.

4. Absorption capacity of DPTD-PAN$_F$

<table>
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<tr>
<th>Adsorbents</th>
<th>Contact time</th>
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<th>$q_e$ (mg/g)</th>
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<td>6.5</td>
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<td>52.91</td>
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3. $^{1}$H and $^{13}$C NMR spectra

**Fig. S3.** $^{1}$H NMR spectra of dimethyl pyridine-2,6-dicarboxylate (2) in CDCl$_3$.

**Fig. S4.** $^{1}$H NMR spectra of pyridine-2,6-dicarboxyhydrazide (3) in DMSO.
Fig. S5. $^1$H NMR spectra of 5,5'-(pyridine-2,6-diyl)bis(1,3,4-thiadiazole-2-thiol) (5) in DMSO

Fig. S6. $^{13}$C NMR spectra of 5,5'-(pyridine-2,6-diyl)bis(1,3,4-thiadiazole-2-thiol) (5) in DMSO
Fig. S7. $^1$H NMR spectra of Dimethyl 2,2'-(2,6-pyridine-diylbis[5,2-(1,3,4-thiadiazole)]thio)]-diacetate (DPTD) in DMSO

Fig. S8. $^{13}$C NMR spectra of Dimethyl 2,2'-(2,6-pyridine-diylbis[5,2-(1,3,4-thiadiazole)]thio)]-diacetate (DPTD) in DMSO
References