Supporting Information

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

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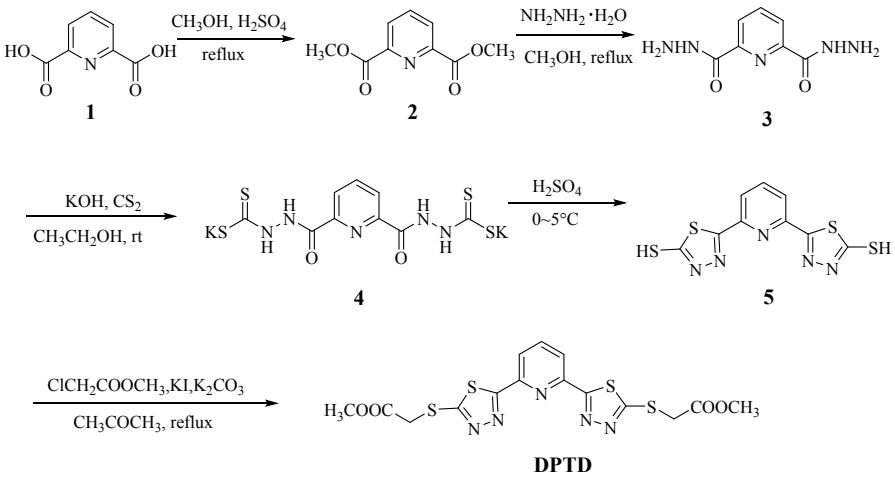
1. Synthesis of DPTD



Scheme 1. The route for synthesis of DPTD

Compound **1** (16.7 g, 100 mmol) was dissolved in MeOH (150 mL). Concentrated H_2SO_4 (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 H_2O (30 mL) and neutralized by the addition of solid K_2CO_3. Then the solution was extracted with EtOAc (2 × 50 mL) and the organic layers were washed with brine, dried over Na_2SO_4 and concentrated to give **2** as a white needle-like crystals, mp 117-118°C (15.6 g, 80%).^{1}H NMR (400 MHz, $CDCl_3$) 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 H_2O (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^{o}C (8 g, 90%). ^{1}H NMR (400 MHz, DMSO-d_6) 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 over night and then gradually added to crush ice. The separated precipitate was filtered off, washed with water, dried, and crystallized from ethanol to give **5** as yellowish powder, mp 288-300^{o}C (4.2 g, 78%).^{1}H NMR (400 MHz, DMSO-d_6) δ 14.92 (s, 2H), 8.27 (d, J = 7.8 Hz, 2H), 8.10 (d, J = 7.8 Hz, 1H). ^{13}C-NMR (400 MHz, DMSO-d_6): 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 K_2CO_3 (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 %). ^{1}H NMR (400 MHz, $CDCl_3$) 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). ^{13}C-NMR (400 MHz, DMSO-d_6): δ 122.58, 140.55, 148.69 (5C, pyrid-C), 169.07, 168.87, 167.09 (3C, thiadiazole ring), 53.17 (2C, CH_3). IR (KBr): v = 3345-3302 (NH), 1662 (C=N), 1660 (C=C), 1242 (C=S) cm^{-1}.

2. Response time of the colorimetric fiber

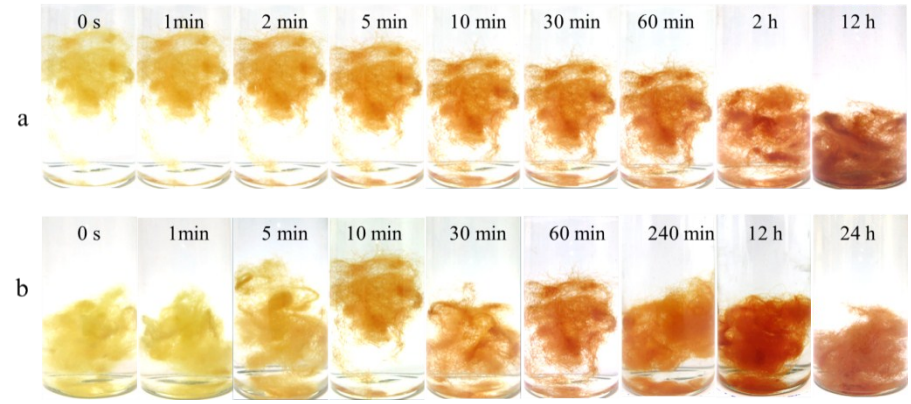


Fig. S1. Response time of DPTD-PAN$_P$F towards Ag^+ with the concentration of (a) 1×10^{-4} mol/L and (b) 1×10^{-5} mol/L.

3. Reusability of the colorimetric fiber

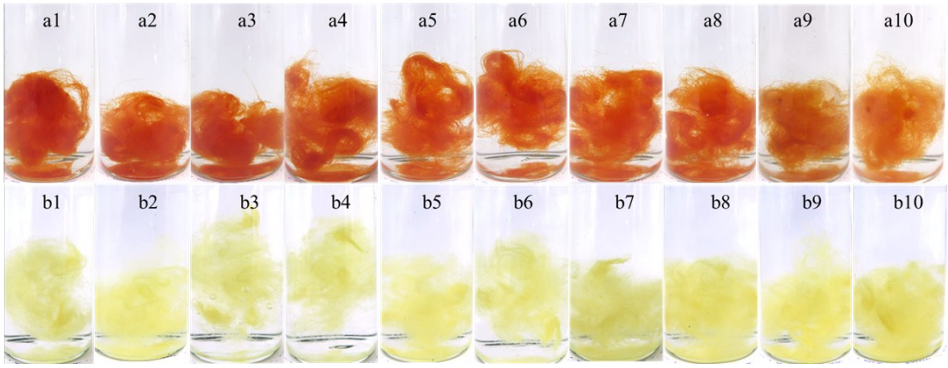


Fig. S2. Reusability of DPTD-PAN$_P$F in water after the 1st-10th (a1-a10) absorption and the 1st-10th (b1-b10) desorption in 1×10^{-5} mol/L Ag^+ solution.

4. Absorption capacity of DPTD-PAN$_P$F

Table S1. Adsorption capacities of some absorbents for Ag^+

Adsorbents	Contact time	pH	q_e (mg/g)	Reference
es-PAN-DNPH	24 h	4.5	6.5	[1]
clinoptilolite	5 min 45 min	4	17 33.23	[2]
brewery's waste biomass	24 h	4	42.72	[3]
chitosan/bamboo charcoal composite beads	180 min	6	52.91	[4]
CS/PVA Imprinted CS/PVA	40 min	6	77.8 125	[5]
MCM-41	60 min	5	92.08	[6]
PAN–TETA	60 min	6	108.14	[7]
Nano-TiO_2-MBI	60 min	6	128.2	[8]
SfGM	60 min	6	137.9	[9]

	5 min		85.32	
DPTD-PAN$_P$F	30 min	5	119.88	This study
	60 min		149.04	

3. ^{1}H and ^{13}C NMR spectra

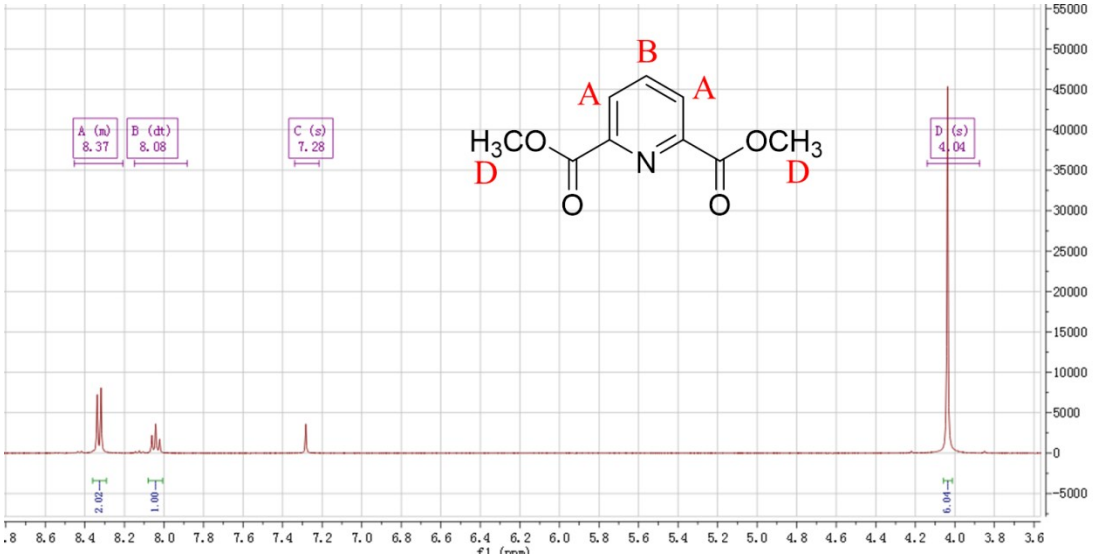


Fig. S3. ^{1}H NMR spectra of dimethyl pyridine-2,6-dicarboxylate (**2**) in $CDCl_3$.

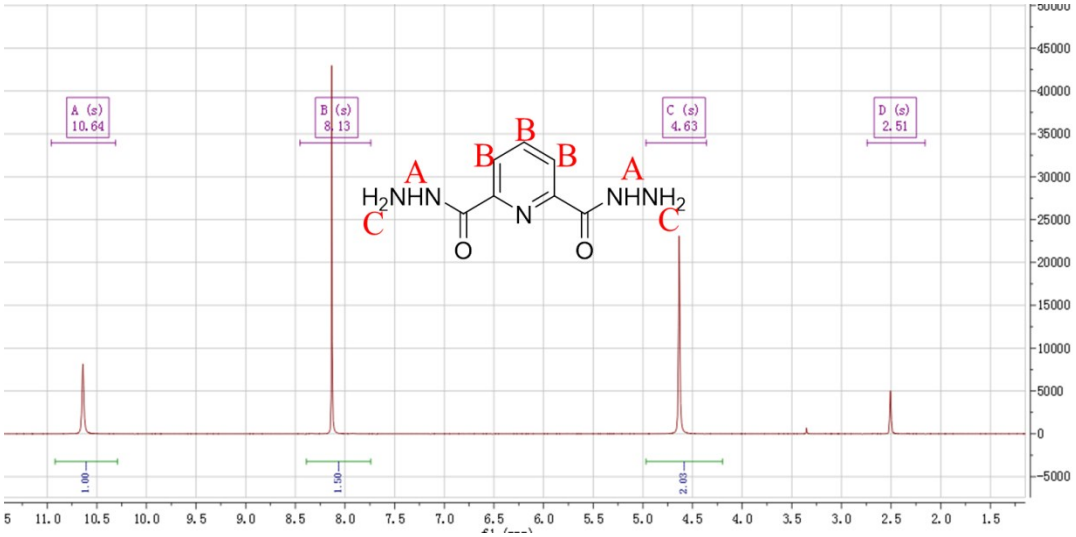


Fig. S4. ^{1}H NMR spectra of pyridine-2,6-dicarbohydrazide (**3**) in DMSO.

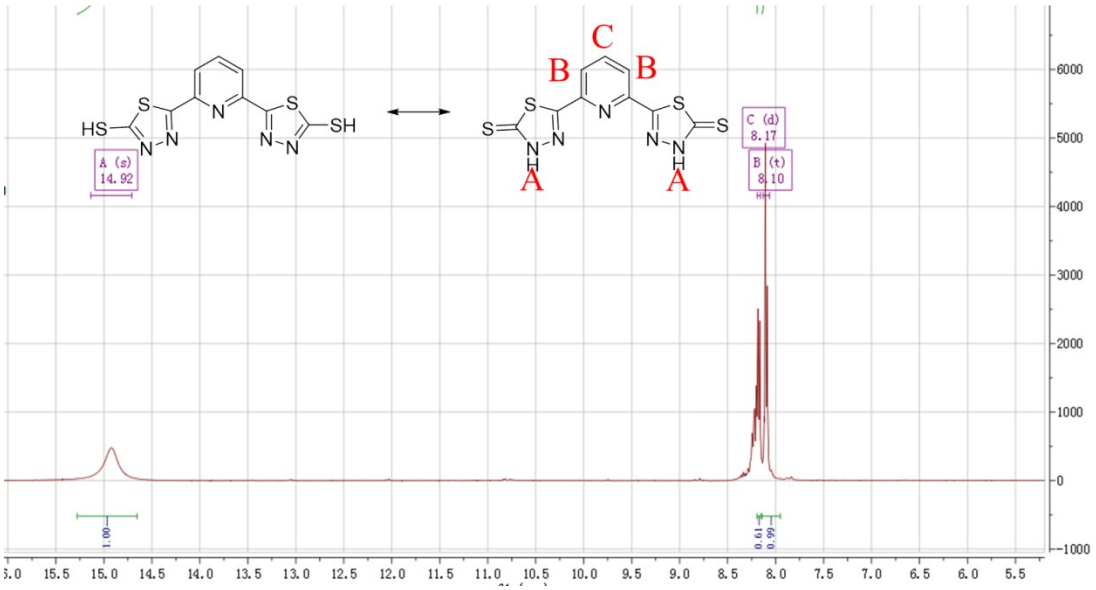


Fig. S5. [1]H NMR spectra of 5,5'-(pyridine-2,6-diyl)bis(1,3,4-thiadiazole-2-thiol) (**5**) in DMSO

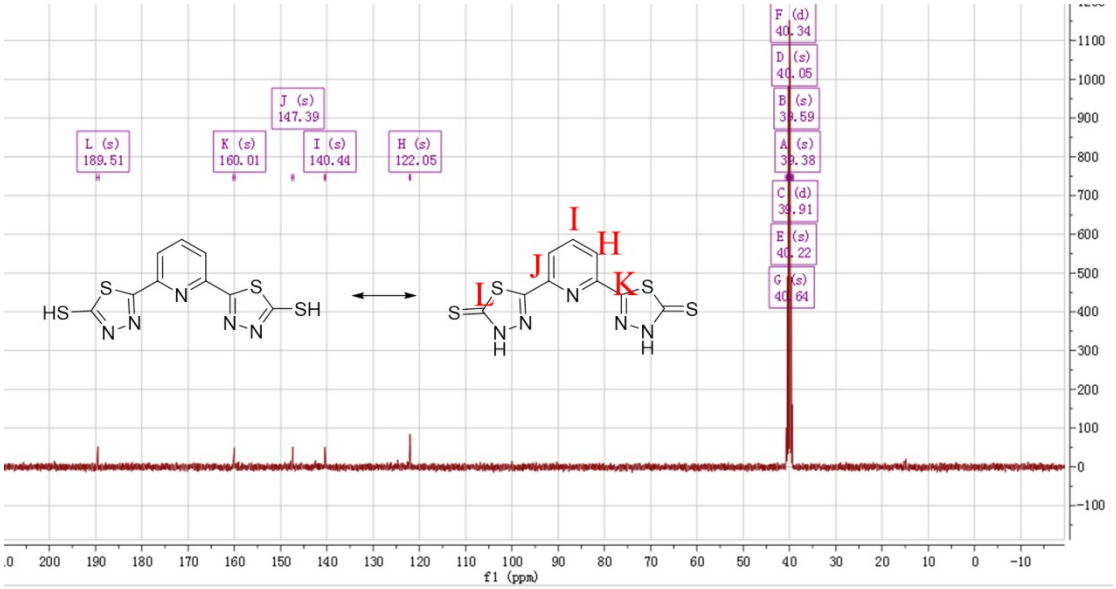


Fig. S6. [13]C NMR spectra of 5,5'-(pyridine-2,6-diyl)bis(1,3,4-thiadiazole-2-thiol) (**5**) in DMSO

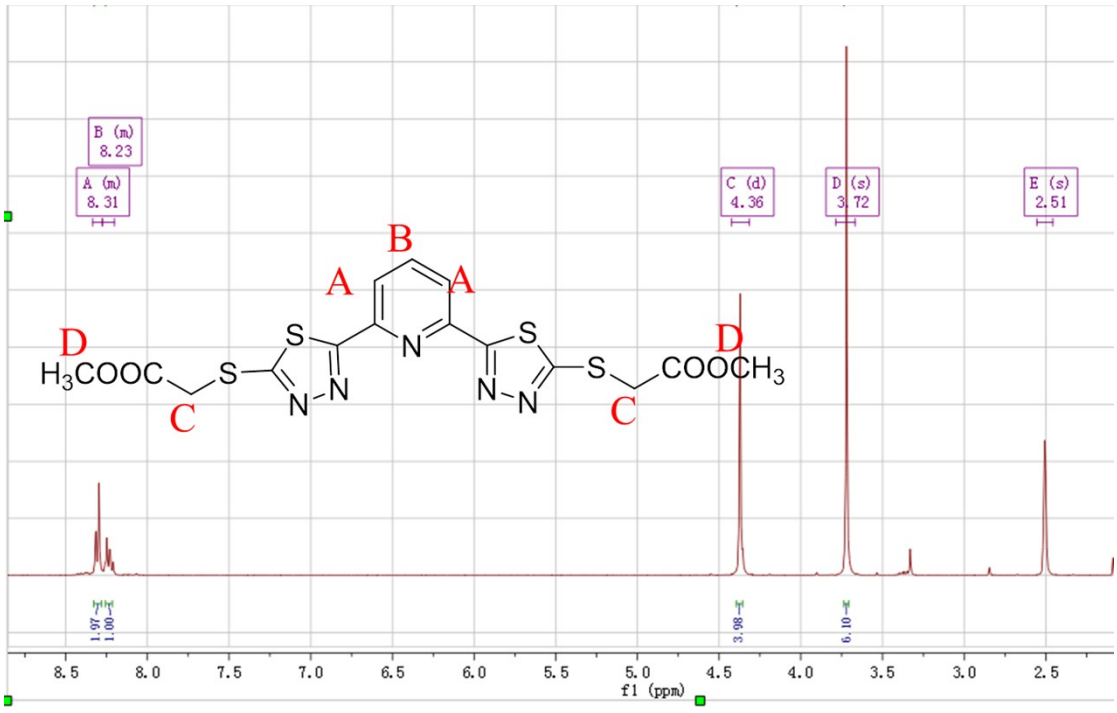


Fig. Fig.S7. [1]H NMR spectra of Dimethyl 2,2'-{2,6-pyridine-diylbis[5,2-(1,3,4-thiadiazolediyl)thio]}-diacetate (DPTD) in DMSO

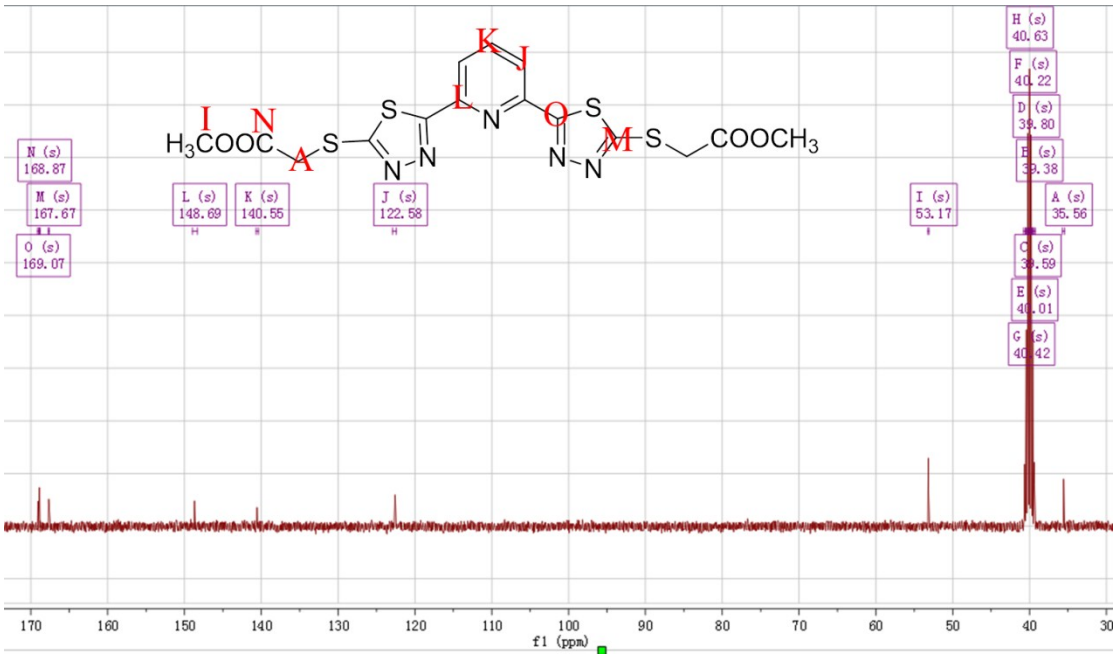


Fig. S8. [13]C NMR spectra of Dimethyl 2,2'-{2,6-pyridine-diylbis[5,2-(1,3,4-thiadiazolediyl)thio]}-diacetate (DPTD) in DMSO

References

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