Electronic Supplementary Information

**Simultaneous removal and conversion of silver ions from wastewater into antibacterial material through selective chemical precipitation**

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**1. Experimental section**

**1.1 Materials and instrumentation**

All chemicals used for the preparation and during the investigation were purchased commercially and used without any further purification. All the metal ions used in this work were provided in the form of nitrate.

NMR spectra measurements were carried out using a Bruker 600 spectrometer at 600 MHz for 1H NMR and 150 MHz for 13C NMR using chloroform-*d* or DMSO-*d6* as the solvents. All chemical shifts are reported in the standard d notation of parts per million. Flourier-transform infrared (FT-IR) spectra was characterized on a Bruker Tensor 27 spectrometer in the range of 4000−500 cm-1, using KBr pellets. Mass spectra were obtained on a Microflex MALDI-TOF mass spectrometer. Elemental analysis was run on a Vario EL III Elemental Analyzer. Single-crystal X-ray diffraction data were collected on an Agilent SuperNova (Dual, Cu at zero, Eos) diffractometer. The crystal was kept at 173.00 (10) K during data collection. The structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using least-squares technique. Energy-dispersive X-ray spectroscopy (EDS) mapping was recorded on a TESCAN LYRA3 XMH field emission scanning electron microscope combined with X-Max-20mm2 spectrometer. X-ray photoelectron spectroscopy (XPS) of the samples was characterized by a Thermo Scientific K-Alpha photoelectron spectrometer using Al Kα radiation and all XPS spectra were referenced to the C 1s neutral carbon peak at 284.8 eV. UV-vis absorption spectra were measured by a HITIACH U-3900 spectrometer.

**1.2 Synthesis**

**Synthesis of 1-CHO (****4-(thiophen-2-yl)benzaldehyde)**

**1-CHO** was synthesized according to the previously reported procedure. 2-Bromothiophene (326 mg, 2 mmol) was treated with 4-formylphenylboronic acid (360 mg, 2.4 mmol) in the presence of Pd(PPh3)4 (0.1 mmol, 116 mg) and 1M aqueous K2CO3 (5 mL) in the medium of THF (20 mL) under N2 atmosphere. After stirred and refluxed for 8 h, the mixture was cooled down to room temperature and extracted with dichloromethane. The organic phase was dried over magnesium sulfate, filtered and concentrated by rotary evaporation. The residue was purified by silicon gel column chromatography with petroleum ether/ethyl acetate (v/v, 10/1) as the eluent to afford compound **1-CHO** as a white solid (310 mg, yield 82%). 1H NMR (600 MHz, chloroform-*d*) δ (ppm) 10.00 (s, 1H), 7.93–7.85 (m, 2H), 7.77 (m, 3H), 7.47 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.40 (dd, *J* = 4.8, 1.2 Hz, 1H), 7.13 (dd, *J* = 5.4, 3.6 Hz, 1H). Anal. Calcd. for C11H8OS: C, 70.19; H, 4.28; O, 8.50; S, 17.03. Found: C, 70.12; H, 4.31; O, 8.52; S, 17.05.

**Synthesis of BTS1 ((*E*)-2-(2-(4-(thiophen-2-yl)benzylidene)hydrazinyl) benzo[d]thiazole)**

A solution of **1-CHO** (188 mg, 1 mmol) and *o*-aminophenol (60 mg, 0.55 mmol) in anhydrous ethanol (20 mL) was stirred and heated at 50 ℃ for 4 h. After cooling to temperature, the mixture was filtered, and the residue thus obtained was washed with ethanol serval times and dried under high vacuum to afford a pale-yellow solid **BTS1** (262 mg, 78.2%).1H NMR (600 MHz, DMSO-*d*6) δ (ppm) 12.32 (s, 1H), 8.15 (s, 1H), 7.79–7.72 (m, 5H), 7.60 (dt, *J* = 4.2, 2.4 Hz, 2H), 7.45 (s, 1H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.18 (dd, *J* = 4.8, 3.6, 1.2 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H). 13C NMR (150 MHz, DMSO-*d*6) δ (ppm) 167.50, 143.22, 135.11, 133.90, 129.15, 127.71, 126.77, 126.45, 126.15, 124.77, 122.10, 122.03. Anal. Calcd. for C18H13N3S2: C, 64.45; H, 3.91; N, 12.53; S, 19.11. Found: C, 64.48; H, 3.92; N, 12.50; S, 19.10. MALDI-TOF: m/z [M]+ cacld. C18H13N3S2, 335.055; found: 336.055.

**Synthesis of 2-CHO ([2,2'-bithiophene]-5-carbaldehyde)**

2-Bromothiophene (326 mg, 2 mmol) was treated with (5-formylthiophen-2-yl) boronic acid (360 mg, 2.4 mmol) in the presence of Pd(CH3COO)2 (0.1 mmol, 42 mg), [(*t*Bu3P)H]BF4 (0.22 mmol, 120 mg) and 1M aqueous K2CO3 (3 mL) in the medium of CH3CN (20 mL) under N2 atmosphere. After stirred and refluxed for 8 h, the mixture was cooled to room temperature and extracted with dichloromethane. The organic phase was dried over magnesium sulfate, filtered and concentrated by rotary evaporation. The residue was purified by silicon gel column chromatography with petroleum ether/ethyl acetate (v/v, 6/1) as the eluent to afford compound **2-CHO** as a yellow solid (296 mg, yield 76%). 1H NMR (600 MHz, DMSO-*d*6) δ (ppm) 9.89 (s, 1H), 7.99 (d, *J* = 4.2 Hz, 1H), 7.71 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.59 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.52 (d, *J* = 4.2 Hz, 1H), 7.19–7.17 (m, 1H). Anal. Calcd. for C9H6OS2: C, 55.64; H, 3.11; O, 8.24; S, 33.01. Found: C, 55.62; H, 3.12; O, 8.26; S, 33.00.

**Synthesis of BTS2 ((*E*)-2-(2-([2,2'-bithiophen]-5-ylmethylene)hydrazinyl)benzo[d] thiazole)**

The synthetic route to **BTS2** was similar to that to **BTS1**,using **2-CHO** as the reactant. The product **BTS2** was afforded as a yellow solid (256 mg, 75.1%). 1H NMR (600 MHz, chloroform-*d*) δ (ppm) 8.38 (s, 1H), 7.80–7.76 (m, 1H), 7.65–7.63 (m, 1H), 7.35 (d, *J* = 5.4 Hz, 1H), 7.31–7.27 (m, 5H), 7.02 (dd, *J* = 6.0, 4.8 Hz, 1H). 13C NMR (150 MHz, DMSO-*d*6) δ (ppm) 167.08, 150.76, 140.31, 138.10, 135.99, 130.49, 128.61, 126.93, 125.98, 124.88, 122.28, 121.57, 118.53. Anal. Calcd. for C16H11N3S3: C, 54.85; H, 3.07; N, 12.80; S, 29.28. Found: C, 54.89; H, 3.03; N, 12.78; S, 29.30. MALDI-TOF: m/z [M]+ cacld. C16H11N3S3, 341.012; found: 343.015.

**Synthesis of BTS3 ((*E*)-4-((2-(benzo[d]thiazol-2-yl)hydrazono)methyl) -*N,N*-diphenylaniline)**

The synthetic route to **BTS3** was similar to that to **BTS1**,using 4-(diphenylamino) benzaldehyde(**3-CHO**) as the reactant. The product **BTS3** was afforded as a yellow solid (288 mg, 68.5%). 1H NMR (600 MHz, chloroform-*d*) δ (ppm) 7.92 (s, 1H), 7.65 (dd, *J* = 7.8, 3.6 Hz, 1H), 7.53–7.50 (m, 3H), 7.32 (td, *J* = 7.8, 15.0 Hz, 1H), 7.29–7.27 (m, 5H), 7.14–7.12 (m, 5H), 7.10–7.04 (m, 4H). 13C NMR (150 MHz, DMSO-*d*6) δ (ppm) 167.30, 150.76, 148.17, 147.38, 145.05, 130.45, 129.32, 128.38, 126.03, 125.85, 125.12, 124.47, 122.28, 121.62, 121.57, 118.53. Anal. Calcd. for C26H20N4S: C, 74.26; H, 4.79; N, 13.32; S, 7.63. Found: C, 74.25; H, 4.80; N, 13.30; S, 7.65. MALDI-TOF: m/z [M]+ cacld. C26H20N4S, 420.141; found: 422.140.

**Synthesis of the complex BTS1-Ag**

The methanol solution of AgNO3 (10 M) was added dropwise into the acetone solution of **BTS1** (0.1 M, 100 mL) at room temperature with thorough stirring in the dark. When no more precipitation formed, the mixture was kept stationary for 30 min, and subsequently filtered. The obtained residue was washed with hot methanol and hot acetone to remove impurities. After dried under high vacuum, the complex **BTS1-Ag** was afforded as a yellow solid and stored away from light to be available for analyses. Anal. Calcd. for C36H26N6S4Ag: C, 55.52; H, 3.37; N, 10.79; S, 16.47; Ag, 13.85. Found: C, 55.50; H, 3.35; N, 10.80; S, 16.49; Ag, 13.86. MALDI-TOF: m/z [M]+ cacld. C36H26N6S4Ag, 778.754; found: 779.750.

**1.3** **General procedures for UV-vis absorption analysis**

The **BTS1** original stock solution (2.5 mM) was prepared in acetone. Stock solutions of various metal ions including Al3+, Fe3+, Co2+, Mg2+, Ni2+, Ag+, Cu2+, Pb2+, Mn2+, Zn2+, K+, Cd2+, Hg2+, Cr3+, Ca2+, Na+ were at 10 mM concentration in deionized water. UV–vis absorption measurements were performed in H2O/acetone (v/v, 99/1) HEPES buffer (10 mM, pH 7.4) solution, unless otherwise specified.

**1.4 Job’s plot**

The experiments of Job’s plot were conducted by using the absorption spectral method. The total concentration of **BTS1** and Ag+ in the solution always kept a constant (25 μM), while the ratio of [Ag+]/([**BTS1**] + [Ag+]) ranged from 0.1 to 0.9 (test at intervals of 0.1). The intensity of maximum absorption peak was recorded to afford the Job’s plot.

**1.5 Calculation of precipitation rate**

The precipitation rate was calculated according to the **Equation S1**,

Where ***Q*** is the precipitation rate (%), ***A0*** is the absorbance intensity at 363 nm of **BTS1** before Ag+ addition, and ***A*** is the absorbance intensity at 363 nm of **BTS1** after Ag+ addition.

**1.6 Antimicrobial activity tests**

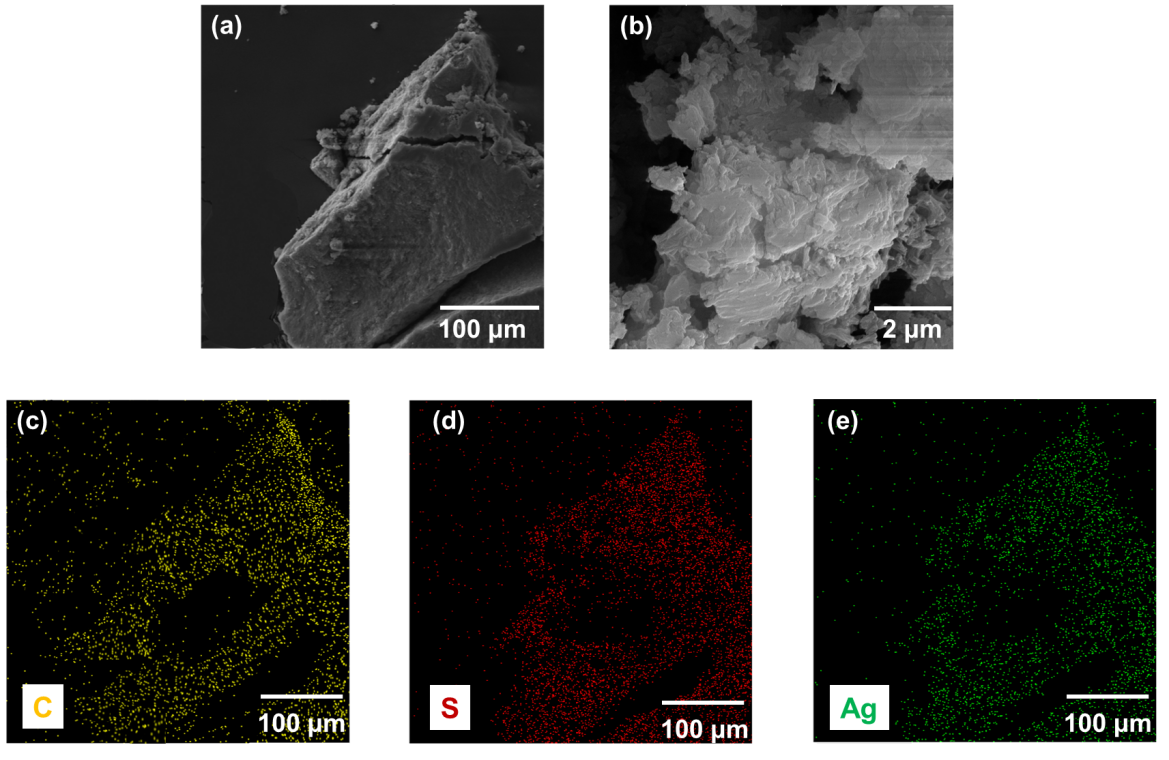
The antimicrobial activities were tested by the conventional disc diffusion methods for gram-positive bacteria (*S. aureus*), and gram-negative bacteria (*E. coli* and *P. aeruginosa*). All the tested compounds including **BTS1** and **BTS1-Ag** were dispersed in anhydrous methanol solution and then loaded on the test circular papers (d = 0.8 cm). The sterilized nutrient agar (NA) and lysogeny broth (LB) were solidified on petri dishes to serve as culture medium for gram-positive bacteria and gram-negative bacteria, respectively. The prepared bacteria (105, 50 μL) were evenly coated on the medium surface. The papers impregnated with the test compound were placed on culture medium followed by inoculation at 37 ℃ for 24 h. Then inhibition zones (DIZ) appeared around the samples were measured in millimeter as antibacterial effect of **BTS1-Ag**. Three times of measurements were averaged.

**2. Figures and Tables**

图表, 直方图

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**Figure S1.** UV-vis absorption spectra of (a) **BTS1** (25 μM), (b) **BTS2** (25 μM) and (c) **BTS3** (25 μM) upon addition of Ag+ (10 mM) in H2O/acetone (v/v, 99/1).



**Figure S2.** SEM images of **BTS1-Ag**: (a) low-magnification and (b) high-magnification; Elemental mapping of **BTS1-Ag** (c-e).

图表, 直方图

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**Figure S3.** UV-vis absorption spectra of (a) **BTS1** (25 μM) and (b) **BTS1-Ag** (adding 10 mM of Ag+) under different pH conditions.

**Table S1.** Crystal data and structure refinement for **BTS1** **CCDC: 2107289**

|  |  |
| --- | --- |
| Identification code | **BTS1** |
| Empirical formula | C18H13N3S2 |
| Formula weight | 335.43 |
| Temperature/K | 293.48(11) |
| Crystal system | monoclinic |
| Space group | C2/c |
| a/Å | 23.480(3) |
| b/Å | 4.5858(8) |
| c/Å | 29.652(4) |
| α/° | 90 |
| β/° | 98.281(13) |
| γ/° | 90 |
| Volume/Å3 | 3159.5(8) |
| Z | 8 |
| ρcalc g/cm3 | 1.410 |
| μ/mm‑1 | 3.060 |
| F (000) | 1392.0 |
| Crystal size/mm3 | 0.05 × 0.02 × 0.01 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 7.61 to 139.62 |
| Index ranges | -28 ≤ h ≤ 26, -5 ≤ k ≤ 3, -36 ≤ l ≤ 33 |
| Reflections collected | 5137 |
| Independent reflections | 2917 [Rint = 0.0555, Rsigma = 0.0814] |
| Data/restraints/parameters | 2917/0/209 |
| Goodness-of-fit on F2 | 1.026 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0725, wR2 = 0.1901 |
| Final R indexes [all data] | R1 = 0.1144, wR2 = 0.2405 |
| Largest diff. peak/hole / e Å-3 | 0.48/-0.45 |

**Table S2.** Crystal data and structure refinement for **BTS2** **CCDC: 2190184**

|  |  |
| --- | --- |
| Identification code | **BTS2** |
| Empirical formula | C16H11N3S3 |
| Formula weight | 341.46 |
| Temperature/K | 300.15(10) |
| Crystal system | monoclinic |
| Space group | P21/c |
| a/Å | 5.39179(11) |
| b/Å | 10.0513(2) |
| c/Å | 28.3981(6) |
| α/° | 90 |
| β/° | 90.9203(18) |
| γ/° | 90 |
| Volume/Å3 | 1538.82(6) |
| Z | 4 |
| ρcalc g/cm3 | 1.474 |
| μ/mm‑1 | 4.386 |
| F (000) | 704.0 |
| Crystal size/mm3 | 0.15 × 0.07 × 0.03 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/° | 6.226 to 154.576 |
| Index ranges | -6 ≤ h ≤ 4, -12 ≤ k ≤ 12, -35 ≤ l ≤ 35 |
| Reflections collected | 9206 |
| Independent reflections | 3069 [Rint = 0.0359, Rsigma = 0.0321] |
| Data/restraints/parameters | 3069/18/199 |
| Goodness-of-fit on F2 | 1.052 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0488, wR2 = 0.1289 |
| Final R indexes [all data] | R1 = 0.0531, wR2 = 0.1317 |
| Largest diff. peak/hole / e Å-3 | 0.33/-0.42 |

**Table S3.** Crystal data and structure refinement for **BTS3** **CCDC: 2107306**

|  |  |
| --- | --- |
| Identification code | **BTS3** |
| Empirical formula | C26H20N4S |
| Formula weight | 420.52 |
| Temperature/K | 293(2) |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 7.8234(6) |
| b/Å | 11.5164(11) |
| c/Å | 13.0798(14) |
| α/° | 66.898(9) |
| β/° | 89.659(8) |
| γ/° | 87.157(7) |
| Volume/Å3 | 1082.50(19) |
| Z | 2 |
| ρcalc g/cm3 | 1.290 |
| μ/mm‑1 | 0.170 |
| F (000) | 440.0 |
| Crystal size/mm3 | 0.11 × 0.05 × 0.04 |
| Radiation | Mo Kα (λ = 0.71073) |
| 2Θ range for data collection/° | 3.85 to 61.708 |
| Index ranges | -9 ≤ h ≤ 10, -15 ≤ k ≤ 14, -18 ≤ l ≤ 16 |
| Reflections collected | 18332 |
| Independent reflections | 5380 [Rint = 0.1174, Rsigma = 0.1390] |
| Data/restraints/parameters | 5380/0/281 |
| Goodness-of-fit on F2 | 0.829 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0762, wR2 = 0.2156 |
| Final R indexes [all data] | R1 = 0.1914, wR2 = 0.3131 |
| Largest diff. peak/hole / e Å-3 | 0.34/-0.27 |

**Table S4.** Antibacterial activity of **BTS1**, **BTS1-Ag** and blank paper.

|  |  |  |  |
| --- | --- | --- | --- |
| **Materials** | **Antibacterial activity (in terms of DIZ in mm)** | | |
| ***S. aureus*** | ***E. coli*** | ***P. aeruginosa*** |
| **Blank** | 8.0 ± 0.15 | 8.0 ± 0.21 | 8.0 ± 0.22 |
| **BTS1** | 8.0 ± 0.25 | 8.0 ± 0.30 | 8.0 ± 0.21 |
| **BTS1-Ag** | 9.9 ± 0.62 | 13.7 ± 0.80 | 10.3 ± 0.68 |

**Table S5.** Antibacterial activity of **BTS1-Ag** at various concentration.

|  |  |  |  |
| --- | --- | --- | --- |
| **Concentration**  **(g/m2)** | **Antibacterial activity (in terms of DIZ in mm)** | | |
| ***S. aureus*** | ***E. coli*** | ***P. aeruginosa*** |
| **4.0** | 11.5 ± 0.78 | 11.6 ± 0.82 | 10.9 ± 0.80 |
| **2.0** | 11.3 ± 0.66 | 11.3 ± 0.70 | 10.8 ± 0.71 |
| **1.0** | 11.0 ± 0.40 | 11.3 ± 0.36 | 10.6 ± 0.62 |
| **0.5** | 9.8 ± 0.36 | 10.2 ± 0.45 | 10.2 ± 0.40 |
| **0.25** | 8.7 ± 0.42 | 9.1 ± 0.38 | 9.5 ± 0.47 |
| **0** | 8.0 ± 0.13 | 8.0 ± 0.20 | 8.0 ± 0.17 |

**3. NMR spectra**

图表

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**Figure S4.** 1H NMR spectra of compound **1-CHO** in chloroform-*d*.

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**Figure S5.** 1H NMR spectra of compound **BTS1** in DMSO-*d*6.

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**Figure S6.** 13C NMR spectra of compound **BTS1** inchloroform-*d*.

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**Figure S7.** 1H NMR spectra of compound **2-CHO** in DMSO-*d*6.

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**Figure S8.** 1H NMR spectra of compound **BTS2** in chloroform-*d*.

图表

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**Figure S9.** 13C NMR spectra of compound **BTS2** inDMSO-*d*6.

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**Figure S10.** 1H NMR spectra of compound **BTS3** in chloroform-*d*.

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**Figure S11.** 13C NMR spectra of compound **BTS3** inDMSO-*d*6.