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Supplementary Information

A Polythiophene-Derived Ratiometric Fluorescent Sensor for Highly Sensitive Determination of Carbenicillin in Aqueous solution

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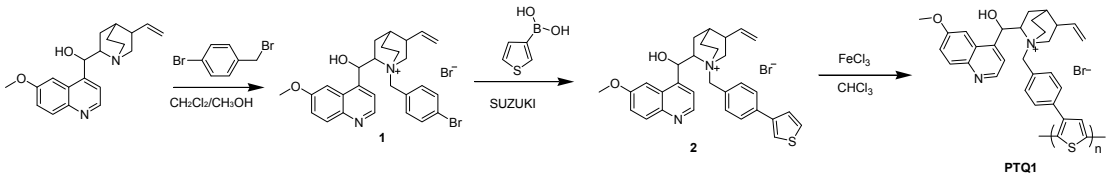
1. Materials and general methods

All UV-Vis and fluorescence spectra in this work were recorded in Hitachi U3010 and Hitachi F-4500 fluorescence spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were determined on a Bruker Advance-400 spectrometer with chemical shifts reported as ppm (tetramethylsilane as internal standard), Matrix Assisted Laser Desorption Ionization-Time of Flight ((MALDI-TOF) Mass Spectra were recorded on a Bruker Microflex mass spectrometer and electrospray ionization (ESI) mass spectra on a Shimadzu LC-MS 2010 instrument. All pH measurements were made with a Sartorius basic pH-meter PB-10. The gel-permeation chromatography was performed using gelatin as the standard, and the CH_3CN-water mixture solution containing $NaNO_3$ (25 mM) was employed as an eluent. TEM images were taken on a JEOL JEM-2100F transmission electron microscope at an acceleration voltage of 150 kV. Dynamic light scattering was performed on Dybapro Nanostar^{TM} from Wyatt Technology Corporation. Zeta potentials were recorded on Zetasize 3000 HS (Malvern, UK).

4-Bromobenzyl bromide, Thiophene-3-boronic acid, Tetrakis(triphenylphosphine)palladium(0), anhydrous quinine, oxalic acid, malonic acid, adipic acid, aspartic acid, glutamic acid, D-tartatic acid, L- tartatic acid, were purchased form Alfa Aesar and used without further purification. streptomycin, chloramycetin, penicillin, neomycin, kanamycin sulfate, erythromycin, amplicillin, carbenicillin disodium were purchased from INALCO. Other reagents were purchased from Beijing Chemical Regent Co. All reagents and chemicals were AR grade and used directly without further purification unless otherwise noted. $CHCl_3$ was distilled from CaH_2 under nitrogen. The water was purified by Millipore filtration system.

2. Synthesis of PTQ1

The overall synthetic pathways was outlined in Scheme **S1** and the details were described below..



Scheme **S1**. Synthetic route of **PTQ1**.

2.1 Synthesis of 1-(4-bromobenzyl)-2-(hydroxy(6-methoxyquinolin-4-yl)methyl)-5-vinyl-1-azonia-bicyclo[2.2.2]-octane bromide (Compound **1**).

Anhydrous quinine (0.64g, 2 mmol) was dissolved in 20 ml of CH_2Cl_2/CH_3OH (v/v = 3/2), then 4-Bromobenzyl bromide (0.5g, 2 mmol) was added. The mixture was stirred at room temperature for 24 hours. After the reaction was complete, the reaction solution was concentrated to 5 ml. The residue was poured into 200 ml of absolute diethyl ether under stirring and then filtered. The crude product was further purified by column chromatography on silica gel (CH_2Cl_2/CH_3OH = 20/1) to give compound **1** (0.9g, yield 78%) as a white solid.

^{1}H NMR (400 MHz, CD_3OD, TMS, ppm): δ 1.55-1.57 (m, 1H), 1.90 (m, 1H), 2.09 (m, 1H), 2.29-2.41 (m, 2H), 2.71-2.73 (m, 1H), 3.35-3.38 (m, 2H), 3.48-3.54 (m, 2H), 3.86-3.90 (m, 1H), 4.05 (s, 3H), 4.35-4.38 (m, 1H), 4.69-4.72(d, 1H), 5.04-5.06 (d, 1H), 5.11-5.16(d, 1H), 5.30-5.34(d, 1H), 5.68-5.77 (m, 1H), 6.61 (s, 1H), 7.40(d, 1H), 7.53-7.56 (d, 1H), 7.59-7.61(d, 2H), 7.75-7.77 (d, 2H), 7.89-7.90 (d, 1H), 8.04-8.06 (d,1H), 8.78-8.79 (d, 1H).
^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 21.3, 24.7, 26.7, 37.7, 46.2, 51.2, 56.2, 60.0, 62.0, 62.3, 64.0, 68.8, 101.9, 117.6, 120.4, 121.2, 125.1, 125.8, 126.1, 131.3, 132.1, 135.4, 136.1, 143.2, 143.7, 146.9, 157.9. ESI-Mass spectra m/z: Calculated: 493.15 (100%), 495.15(97.4%); Found: 493.3, 495.3.

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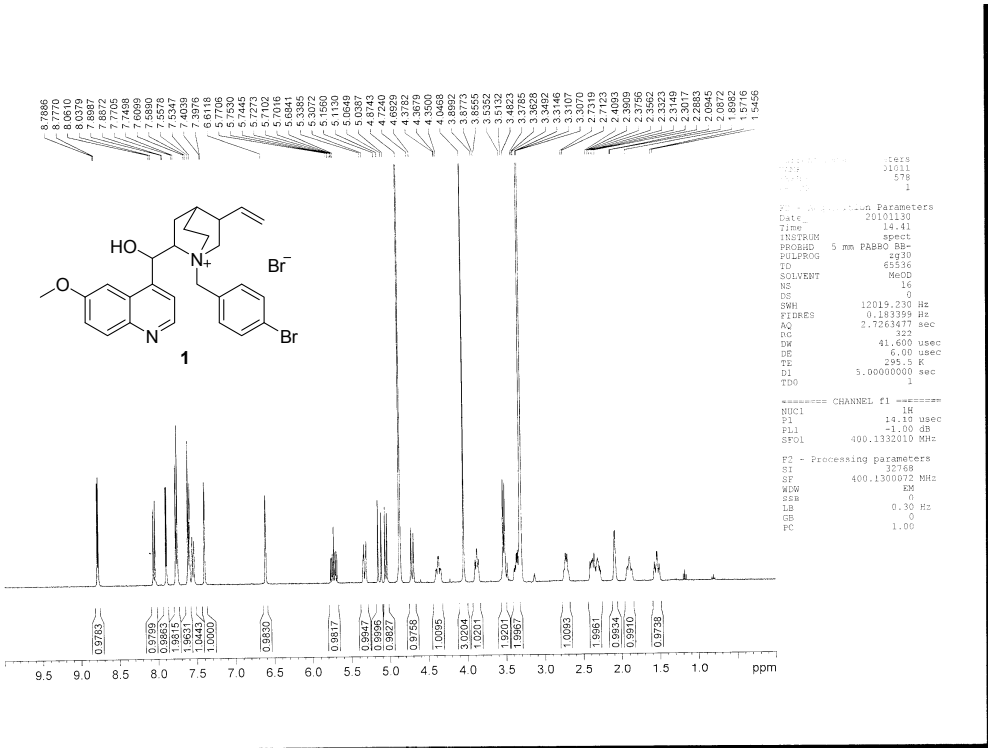

Fig. **S1**. ^{1}H NMR of compound **1**. (solvent: CD_3OD)

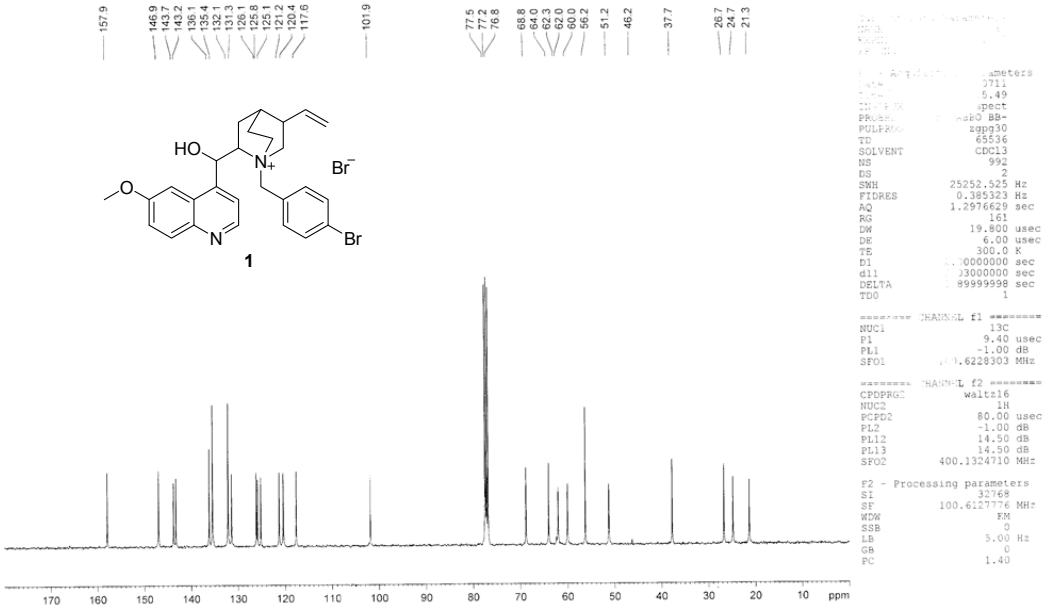

Fig. **S2**. ^{13}C NMR of compound **1**. (solvent: $CDCl_3$)

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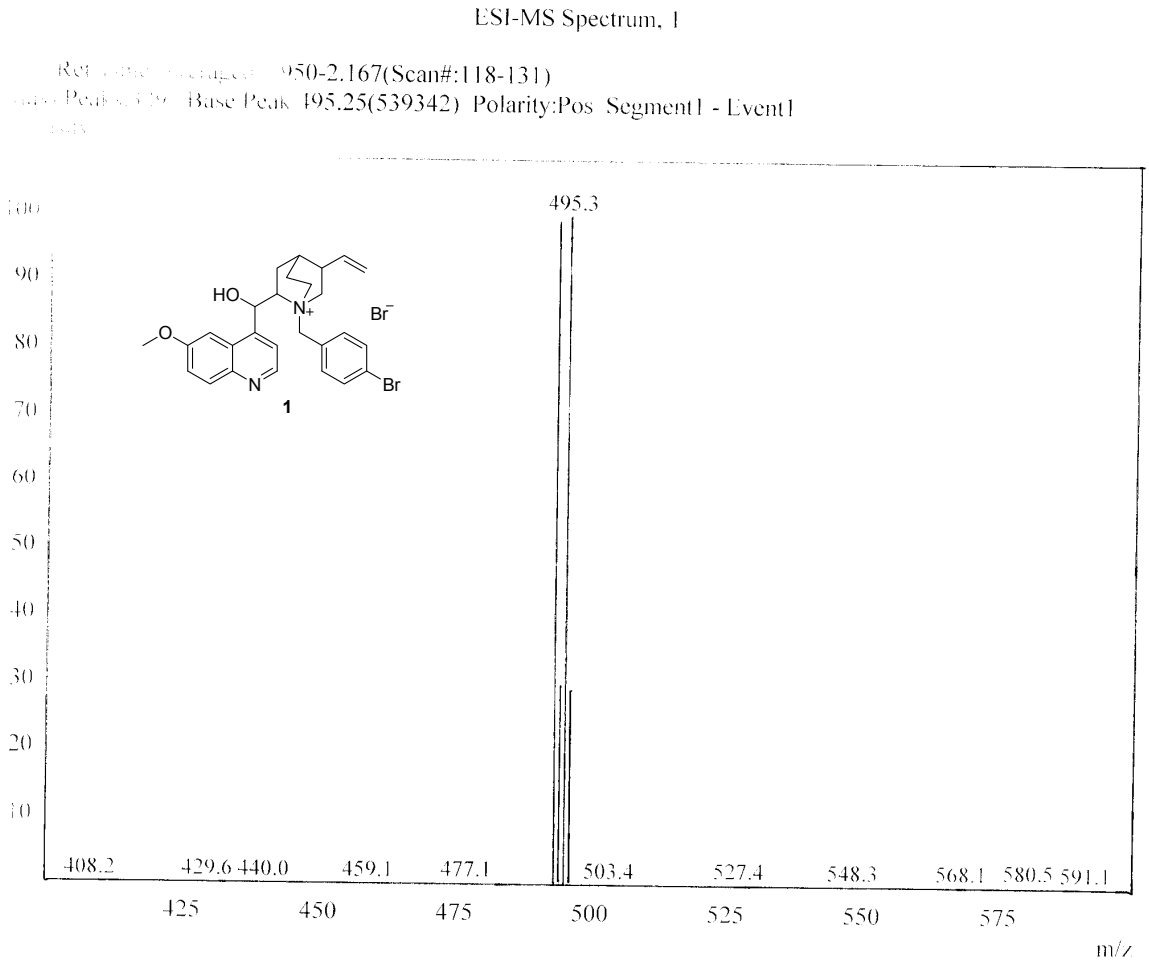

Fig. **S3**. ESI-MS of compound **1**.

2.2 Synthesis of 2-(hydroxy(6-methoxyquinolin-4-yl)methyl)-1-(4-(thiophen-3-yl)benzyl)-5-vinyl-1-azonia-bicyclo[2.2.2]octane bromide (Compound **2**)

To a mixture of compound **1** (0.58g, 1 mmol), Na_2CO_3 (0.5g, 4.7 mmol), $Pd(PPh_3)_4$ (200 mg, 0.17 mmol), Thiophene-3-boronic acid (0.15g, 1.17 mmol) in 20 ml EtOH under nitrogen was added deionized water (10 ml) by syringes. After refluxing at 90 ^{0}C for 10 hours, EtOH was removed under reduced pressure. The residue solution was extracted with 3 × 20 ml CH_2Cl_2. The collected organic layer was dried with $MgSO_4$. The solution was concentrated to 5 ml. The residue was poured into 200 ml of absolute diethyl ether under stirring and then filtered. The curded product was further purified by column chromatography on silica gel (CH_2Cl_2/CH_3OH = 20/1) to give compound **2** (0.4g, yield 70%) as a colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$, TMS, ppm): δ1.51-1.52 (m, 1H), 1.74 (m, 1H), 2.03 (m, 1H), 2.24-2.32 (m, 2H), 2.58 (m, 1H), 3.16-3.18 (m, 1H), 3.54-3.56 (m, 1H), 3.59 (m, 1H), 3.83-3.85 (m, 1H), 3.93 (s, 3H), 4.84-4.87 (d, 1H), 5.01-5.15(m, 3H), 5.56-5.61 (m, 1H), 6.14-6.17(d, 1H), 6.68-6.76 (m, 2H), 7.30-7.34 (m, 3H), 7.40-7.42 (m, 1H), 7.45-7.47 (m, 1H), 7.54-7.57 (m, 2H), 7.75-7.80 (m, 3H), 7.99-8.02 (d, 1H), 8.71-8.73 (d,1H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS, ppm): δ 21.8, 25.0, 26.9, 30.9, 38.2, 51.3, 56.5, 61.0, 63.4, 64.4, 69.4, 102.4, 118.1, 120.6, 121.0, 121.7, 125.5, 126.1, 126.2, 126.9, 131.9, 134.4, 136.5, 137.9, 140.8, 143.5, 144.1, 147.5, 158.2. MALDI-TOF Mass spectra m/z: Calculated: 497.67; Found: 497.63.

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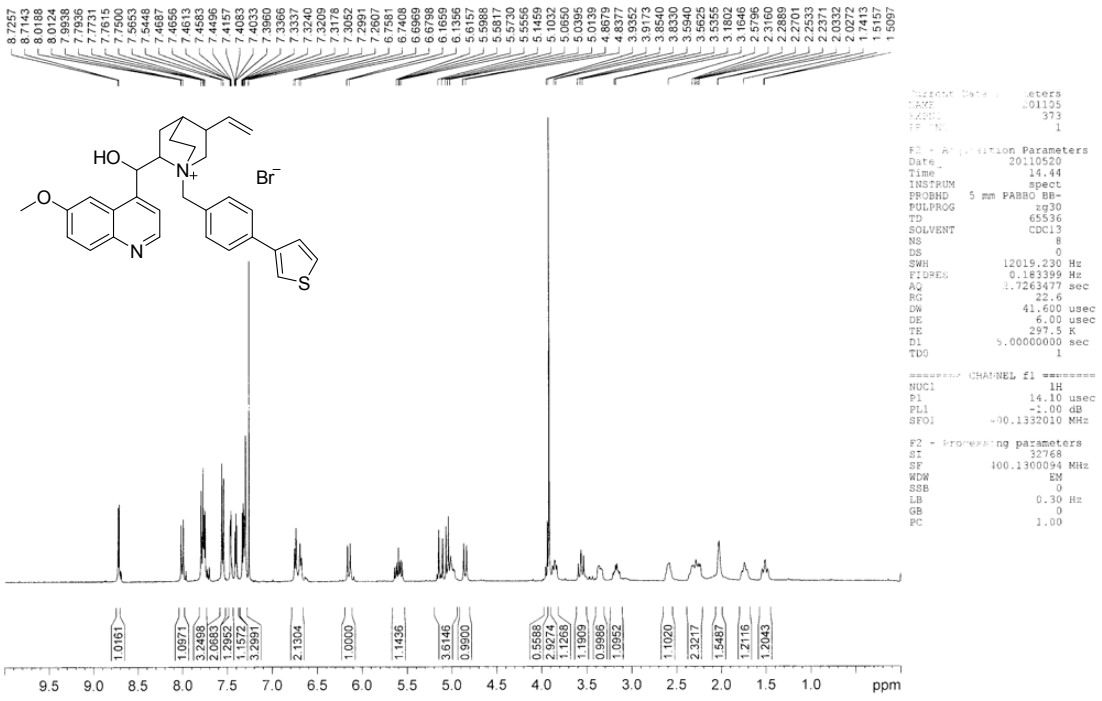

Fig. **S4**. ^{1}H NMR of compound **2**. (solvent: $CDCl_3$)

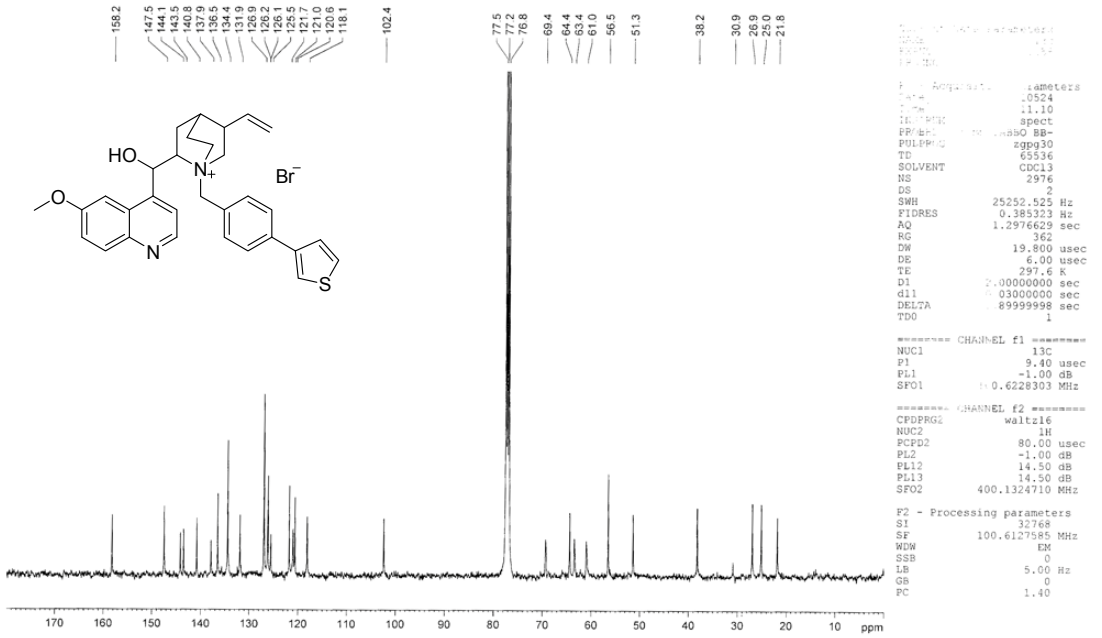

Fig. **S5**. ^{13}C NMR of compound **2**. (solvent: $CDCl_3$)

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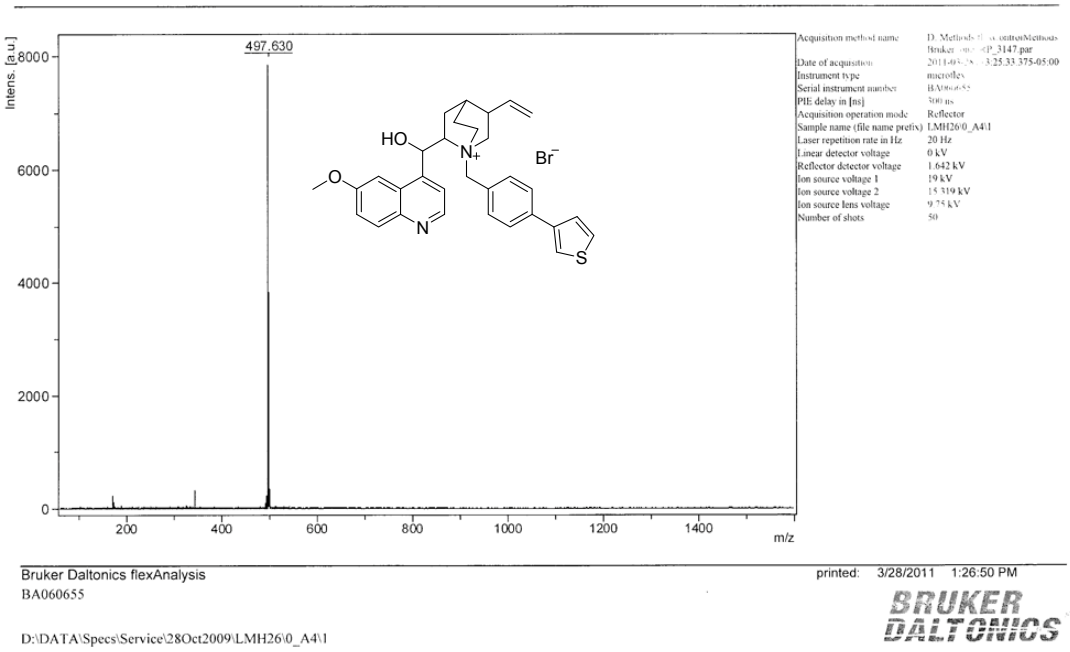

Fig. **S6**. MALDI-TOF-MS of compound **2**.

2.3 Synthesis of the **PTQ1**

PTQ1 was prepared *via* an oxidative polymerization under nitrogen in the presence of $FeCl_3$. 4 equiv of $FeCl_3$ was dissolved in 30 ml of dry $CHCl_3$ under nitrogen, and then 1 equiv of compound **2** was dissolved in 20 ml of $CHCl_3$ and added drop wise. The reaction mixture was stirred at room temperature for 2 days. The resulting precipitate was collected, washed with a mount of methanol, and finally dried under vacuum to give the desired polymers as a dark red solid.

PTQ1 (yield: 65%) Gel-permeation chromatography analysis (GPC): *Mn*=31,900 g mol^{-1}, PDI=1.162.

^{1}H NMR (400 MHz, DMSO-d6, TMS, ppm): δ 1.06 (s, br), 1.23 (s, br), 1.41 (s, br), 1.76 (s, br), 2.07 (s, br), 2.31 (s, br), 3.44 (s, br), 3.96 (s, br), 4.91-4.99 (d, br), 5.63-5.71 (d, br), 6.59 (s, br), 7.16 (s, br), 7.39-7.52 (br), 7.89 (s, br), 8.07 (s, br), 8.85 (s, br).

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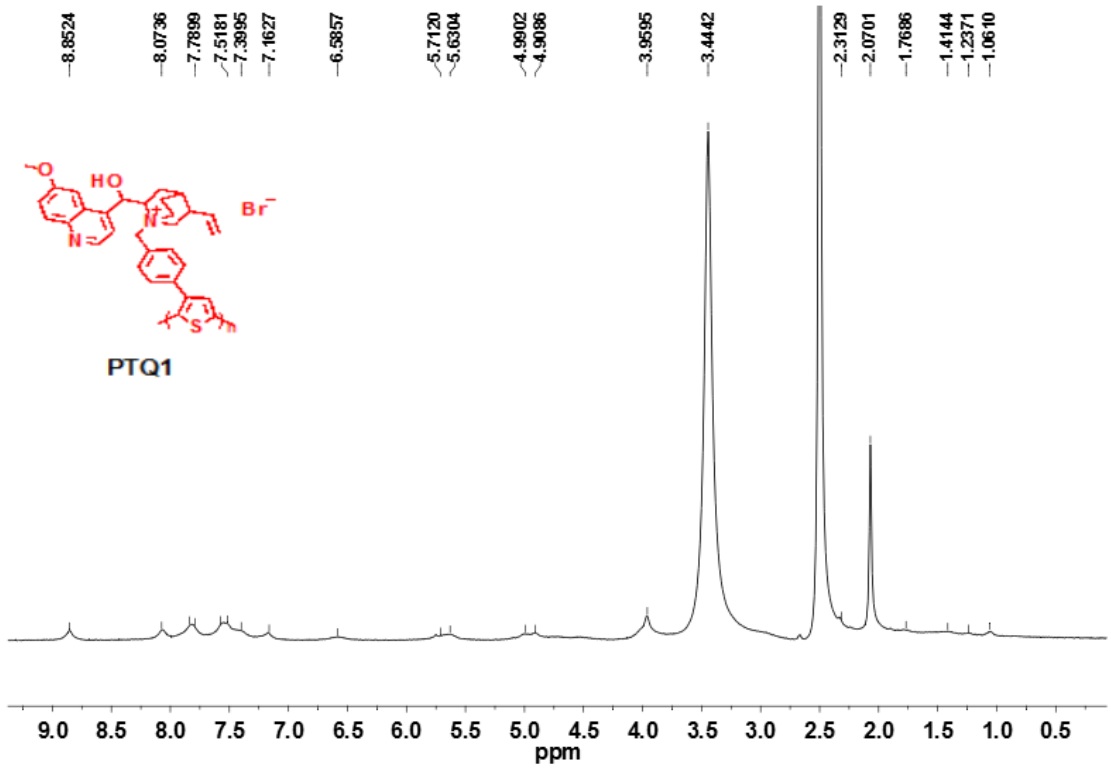

Fig. **S7**. ^{1}H NMR of **PTQ1**. (solvent: DMSO-d_6)

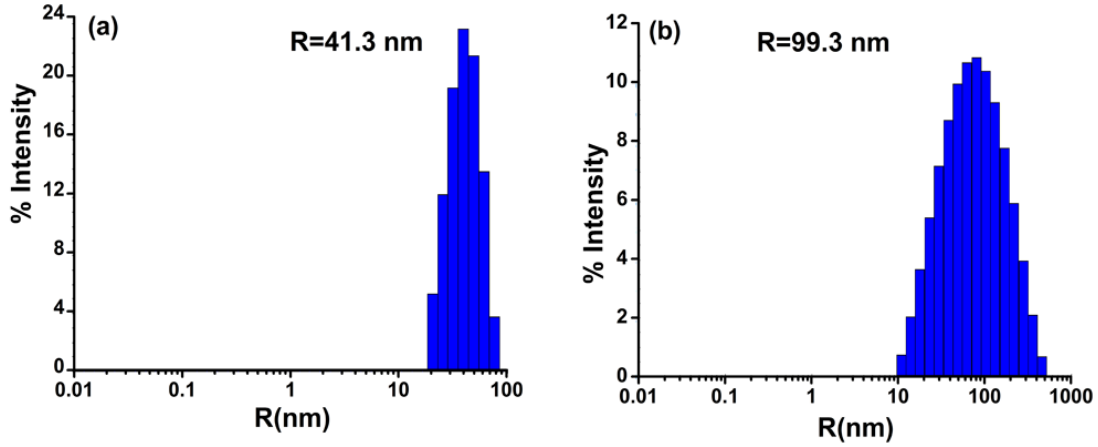

Fig. S8. DLS of PTQ**1** (75 μM) in 10 mM HEPES buffer solution (1% CH_3CN, pH = 7.4) in the absence (a) and presence (b) of 7.5 μM Carbenicillin.