Electronic Supplementary Material (ESI) for Polymer Chemistry

Supplementary Information

Novel electrochemical and pH stimulus-responsive supramolecular polymer with disparate pseudorotaxanes as relevant unimers†

Xiang Ma, Ruyi Sun, Weifeng Li, and He Tian*

Key Laboratory for Advanced Materials and Institute of Fine Chemicals
East China University of Science & Technology, Shanghai 200237 (P.R. China)
E-mail: tianhe@ecust.edu.cn, fax: +86-21-64252288.

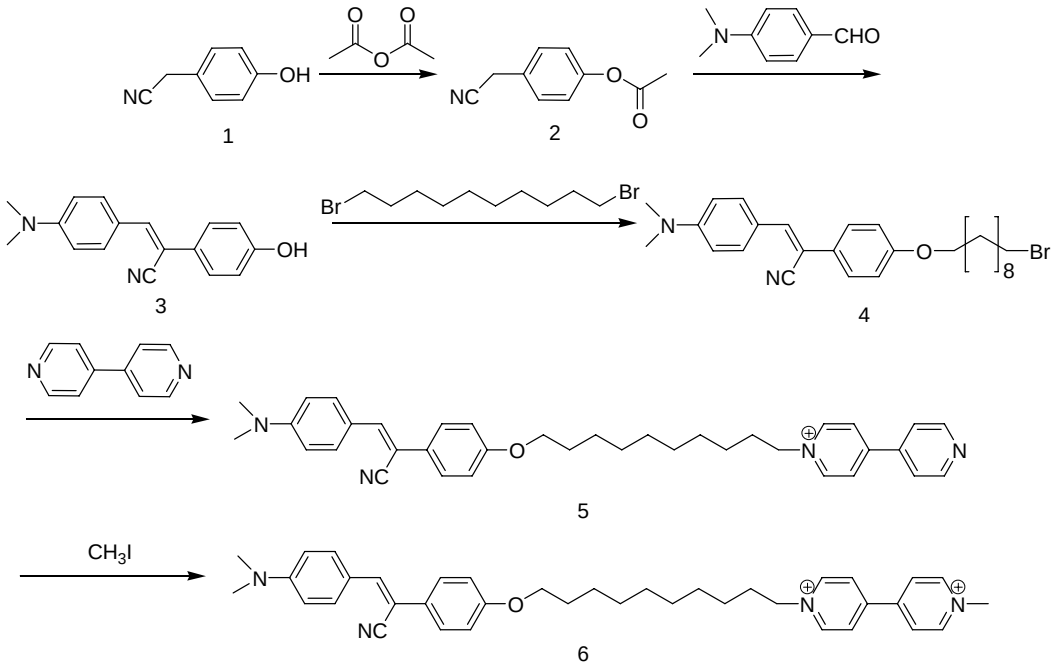
Experimental

Instruments

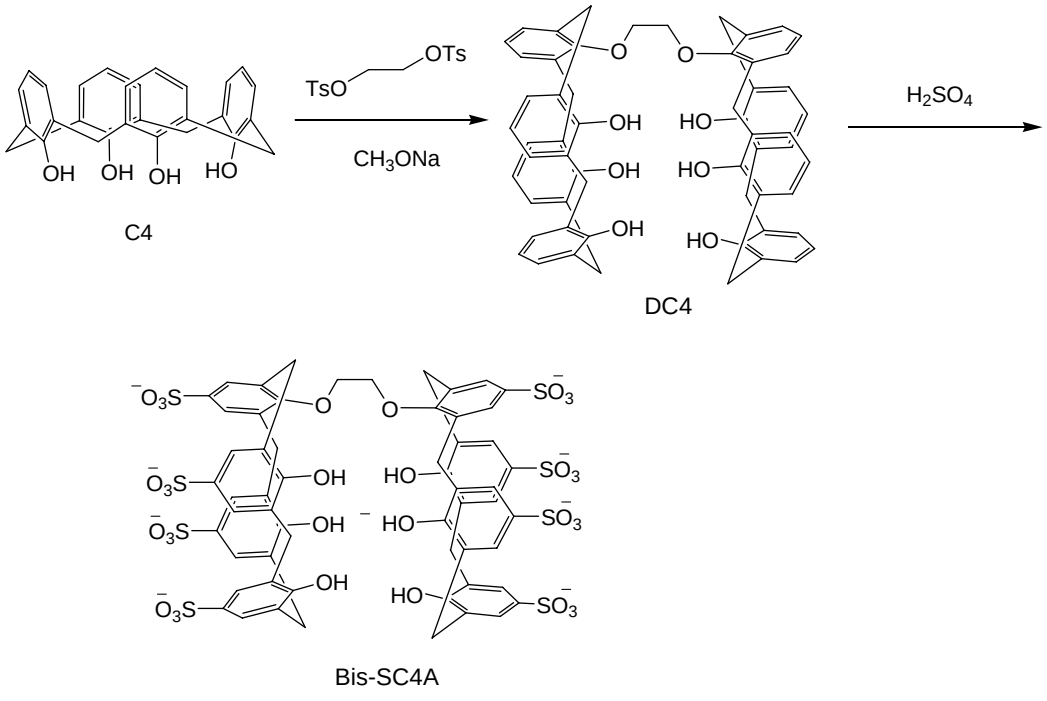
^{1}H NMR spectra and the ^{13}C NMR spectra were measured on a Brüker AV-400 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a HP5989 mass spectrometer. UV-vis spectra were obtained on a Varian Cary 100 spectrophotometer (10cm quartz cell used). Fluorescent spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer. The ICD spectra were done on a Jasco J-815 CD spectrophotometer in a 10 cm quartz cell. The dynamic light scattering (DLS) was performed on a laser light scattering spectrometer (ALV/CGS-5022F). Atomic force microscopy (AFM) was carried out using AJ-III AFM microscope at room temperature, and samples were prepared by spin coating an DMSO solution on mica. SEM was performed using SEM (JSM-6360LV) EDS (Falcon) SEM microscope at room temperature, and the samples were prepared by coating on glass. The cyclic voltammetry (CV) measurements were carried out on a CHI660C electrochemical analyzer. All solutions were prepared in 0.1 M $TBAClO_4$ at room temperature, and deoxygenated by purging with dry nitrogen for at least 15 min before each experiment. The glassy carbon working electrode was polished to a mirror with 0.05 nm BAS alumina suspension on a brown texmet polishing pad, sonicated in

distilled water for a few minutes to remove any residual alumina particles. A platinum wire was used as the counter electrode. The measured potentials were recorded with respect to an Ag/AgCl reference electrode.

Preparation of Compounds [1, 2]



Scheme S1. Synthetic route to the precursor **K** (the Br^-, I^- is overleapt here).



Scheme S2. Synthetic route to **Bis-SC4A** (the $8Na^{4+}$ is overleapt here), the synthesis see reference 2 (*Chem. Commun.*, 2010, 2620).

Synthesis of the precursors

1. *1-(4-nitro-10-N,N-dimethylaminodiphenylvinylphenol)-10-bromodecane **4***

Compound 3-(4-(dimethylamino)phenyl)-2-(4-phenol)acrylonitrile (2.9 g, 11mmol), 1,10-dibromodecane 33 g (110 mol), K_2CO_3 3.0 g (22mmol), and 18-crown-**6** (0.2 g) were mixed in acetone (30 mL). The mixture was refluxed for 8 h and then poured into alcohol (100 mL). Concentrate the solution under vacuum pressure till there was 60ml mixture left. The crude produce was provided under ultrasound wave. The precipitate was filtered and washed with petroleum ether. The crude solid was dried and then washed with water and dried to give **4** 4.5 g (84.9% yield). ^{1}H NMR ($CDCl_3$): *d* [ppm]: 7.82 (d, 2H), 7.54 (d, 2H), 7.29 (s, 1H), 6.92 (d, 2H), 6.72 (d, 2H), 3.98 (m, 2H), 3.41 (m, 2H), 3.05 (s, 6H), 1.85 (m, 4H), 1.31 (m, 12H).

2. *1-(4-nitro-10-N,N-dimethylaminodiphenylvinylphenol)-10-(4-(4'-pyridyl)pyridiniu m)-decanylbromide **5***

A solution of compound **4** (6 g, 12.4 mmol) and 4,4′-bipyridine (11.6 g, 74.4 mmol) in acetonitrile (60 mL) was stirred for 24 h at 80 °C. The precipitate was collected by concentration under vacuum pressure and applied to silica gel chromatography (dichloromethane: methanol = 50:3) to provide compound **5** (5.2 g, 66% yield). ^{1}H NMR ($CDCl_3$): *d* [ppm]: 9.52 (d, 2H), 8.83 (d, 2H), 8.37 (d, 2H), 7.80 (d, 2H), 7.73 (d, 2H), 7.53 (d, 2H), 7.29(s, 1H), 6.90 (d, 2H), 6.70 (d, 2H), 4.95 (m, 2H), 3.96 (s, 6H), 2.90 (m, 2H), 2.03 (m, 2H), 1.75 (m, 4H), 1.32 (m, 10H). ^{13}C-NMR（$CDCl_3$）159.2, 153.5, 151.4, 150.6, 145.7, 140.8, 131.7, 130.8, 130.2, 127.7, 126.6, 125.9, 121.7, 119.7, 114.9, 111.5, 68.1, 61.7, 40.0, 31.7, 29.2, 26.1, 25.8.

3. *1-(4-nitro-10-N,N-dimethylaminodiphenylvinylphenol)-10-(4-(4'-methyl-pyridyl)p yridinium)-decanyldihaloid **6***

A solution of compound **5** (0.3 g, 0.47 mmol) and iodomethane (0.54 g, 3.77 mmol) in acetonitrile (30 mL) was stirred for 24 h at 60 °C. After removing the acetonitrile, diethyl ether was added to the resulting solution to induce precipitation. The precipitate was collected by filtration and washed with petroleum ether to provide the compound **6** (0.31 g, 83% yield). ^{1}H NMR (DMSO-d_6): *d* [ppm]: 9.40 (d, 2H), 9.30 (d, 2H), 8.79 (dd, 4H), 8.09 (m, 1H), 7.91 (d, 1H), 7.71 (d, 2H), 7.43 (d, 2H), 7.29 (s, 1H),

7.04 (dd, 2H), 4.69 (s, 1H), 4.44 (s, 2H), 4.01 (d, 1H), 3.65 (s, 2H), 3.56 (s, 2H), 2.86 (s, 3H), 1.98 (s, 1H), 1.78-1.66 (m, 1H), 1.32 (d, 8H). ^{13}C-NMR（$CDCl_3$）159.9, 159.4, 148.4, 148.0, 146.5, 145.7, 137.9, 135.4, 130.2, 127.6, 126.6, 126.0 120.9, 115.1, 112.1, 67.8, 60.8, 56.3, 48.1, 30.7, 28.7, 28.6, 28.4, 25.4. MS (ESI): m/z=279.1713 [**6**-2Br$^-$-2I$^-$-CH_3-H]$^{2+}$.

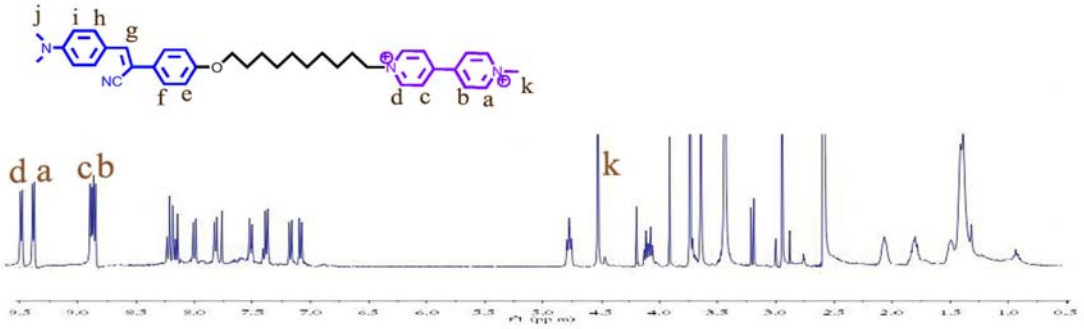


Figure S1 ^{1}H NMR spectrum of **K** in DMSO-d_6 (400MHz, the Br$^-$, I$^-$ is overleapt here and in all the following Figures for clarity).

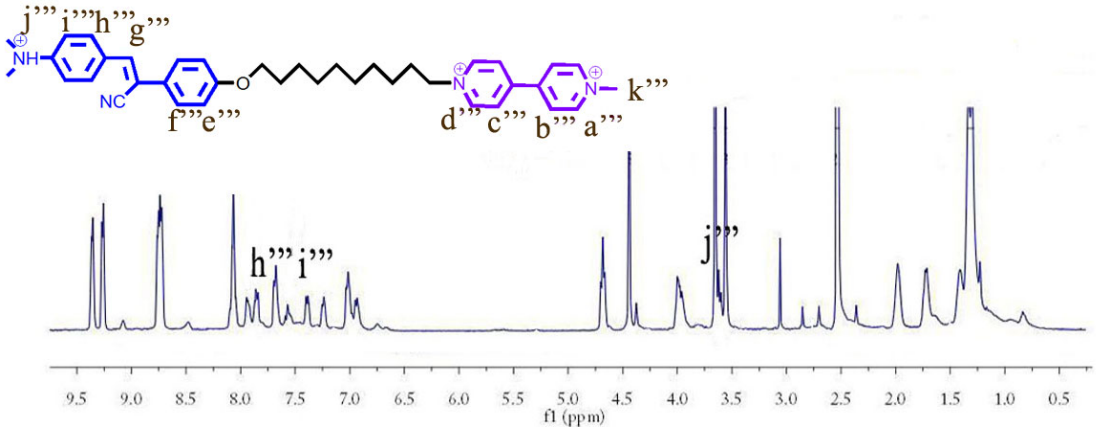


Figure S2 ^{1}H NMR spectrum of **K-H** in DMSO-d_6 (400MHz)

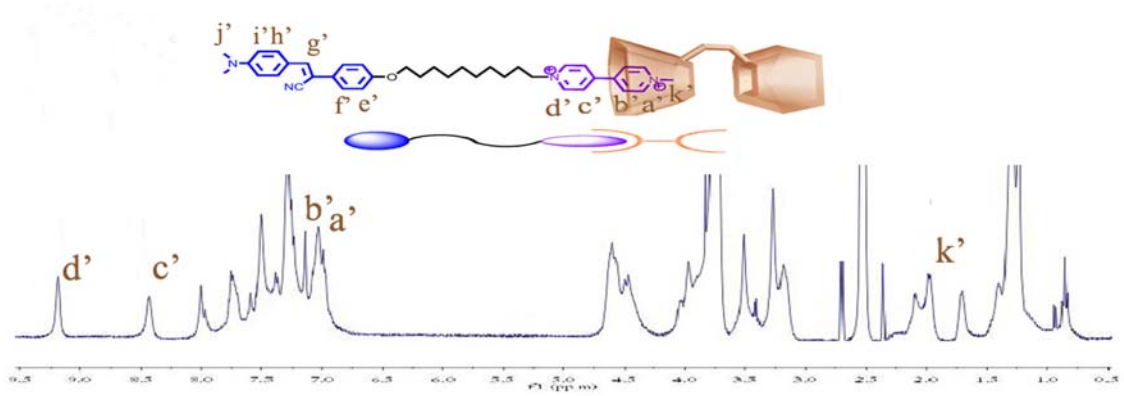


Figure S3 ^{1}H NMR spectrum of **R1** in DMSO-d_6 (400MHz). [2]

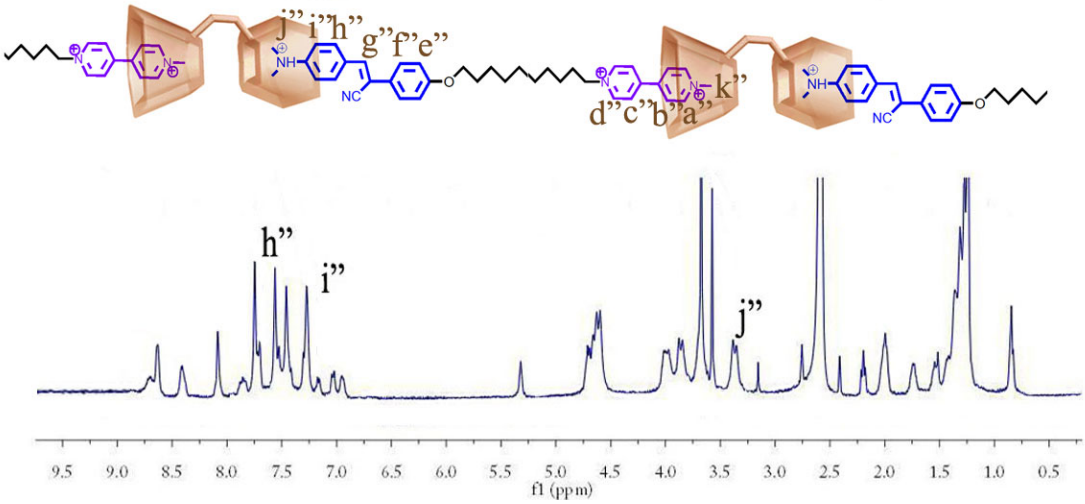


Figure S4 ^{1}H NMR spectrum of **P** in DMSO-d_6 (400MHz).

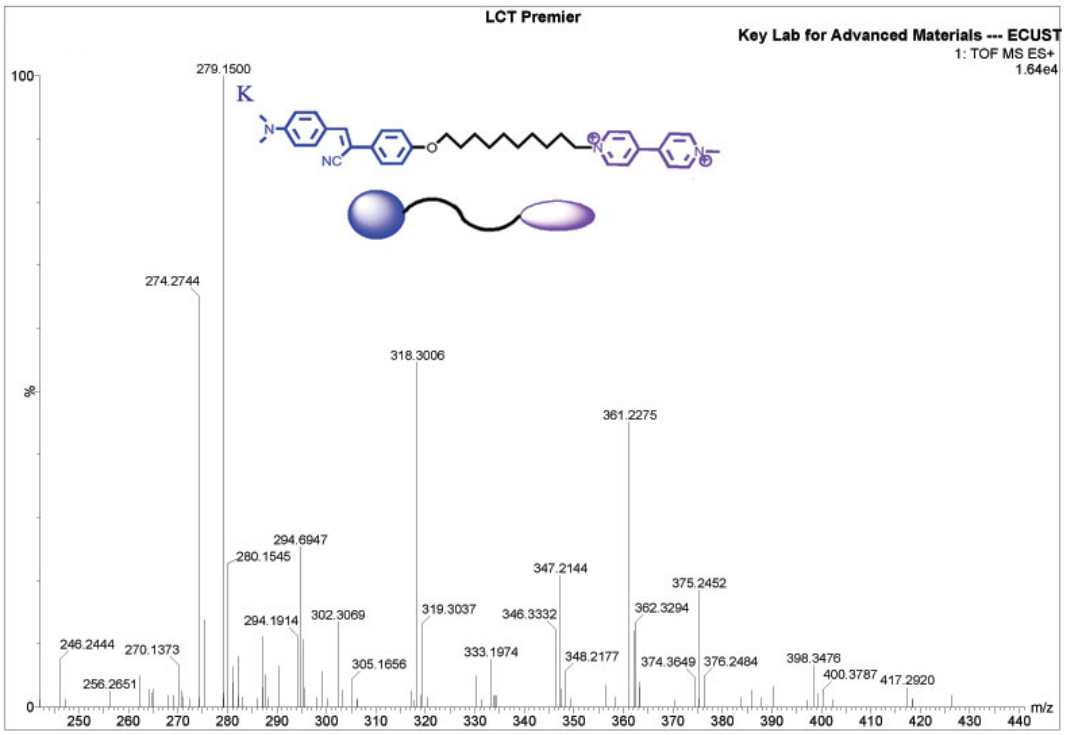


Figure S5. MS spectrum (ESI) of **K**

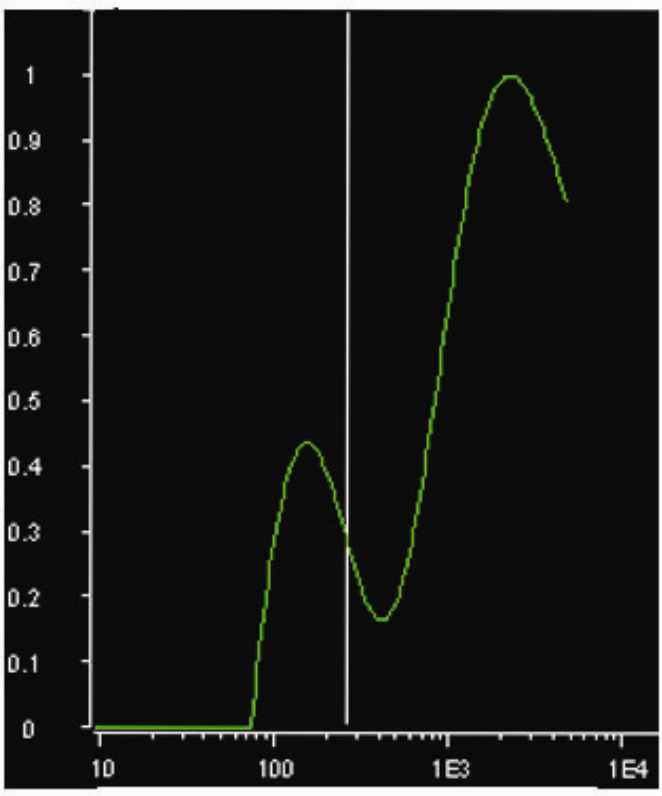


Figure S6. Distribution of the hydrodynamic diameter of the polymer P.

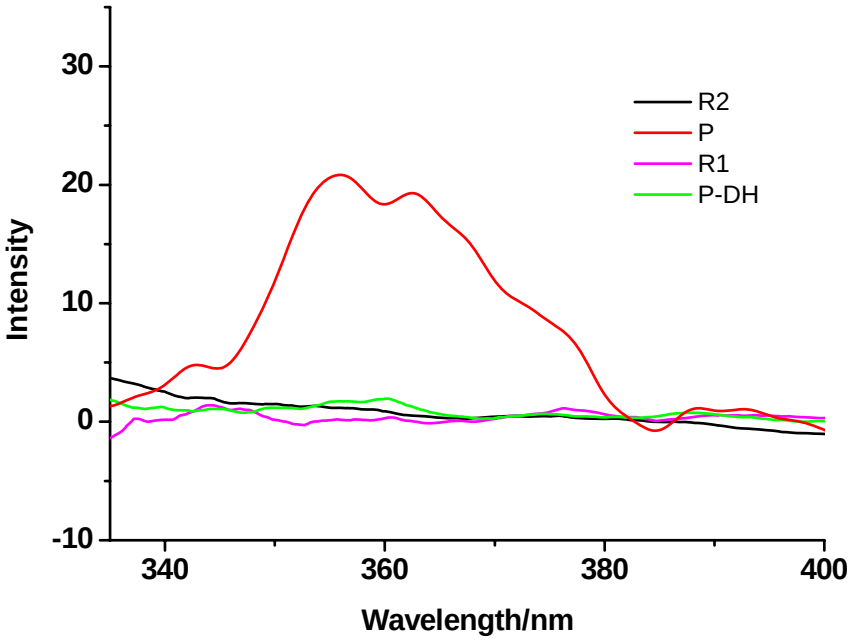


Figure S7. The ICD spectra of pseudorotaxane1 **R1**, supramolecular polymer **P**, pseudorotaxane 1 **R2** and pseudorotaxane **P-DH** (deprotonation of **P**, similar with **R1**)

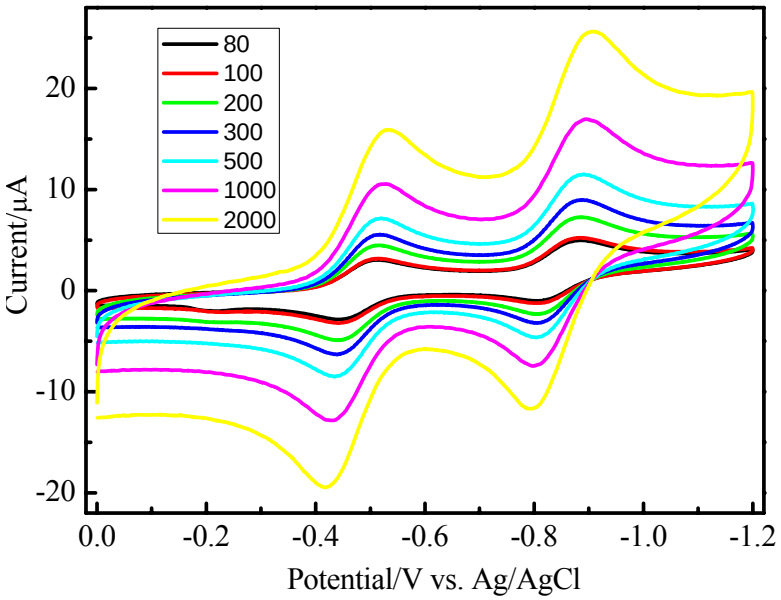


Figure S8. Cyclic voltammetric curves of **K** recorded in 2×10^{-4} M DMSO solution containing 0.1 M $TBAClO_4$, as a function of scan rate (80-2000 $mV\cdot s^{-1}$).

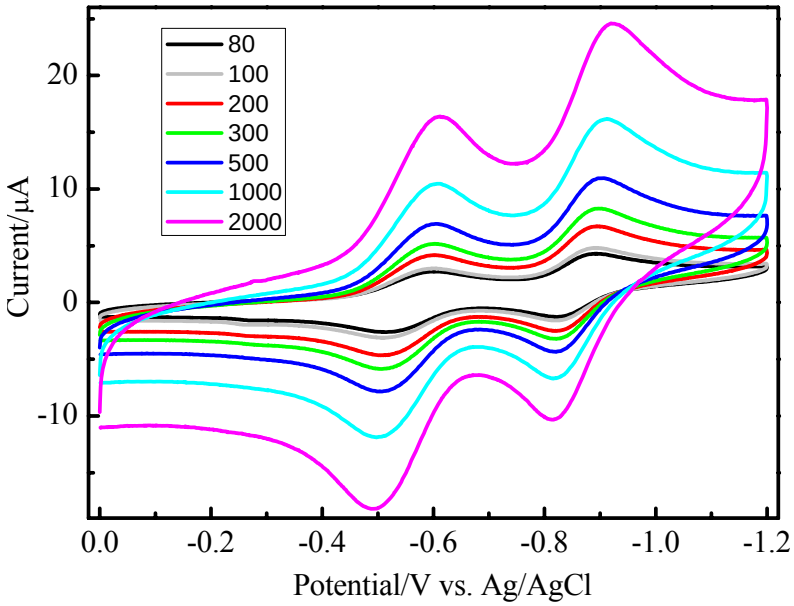


Figure S9. Cyclic voltammetric curves of **R1** recorded in 2×10^{-4} M DMSO solution, containing 0.1 M $TBAClO_4$, as a function of scan rate (80-2000 $mV\cdot s^{-1}$).

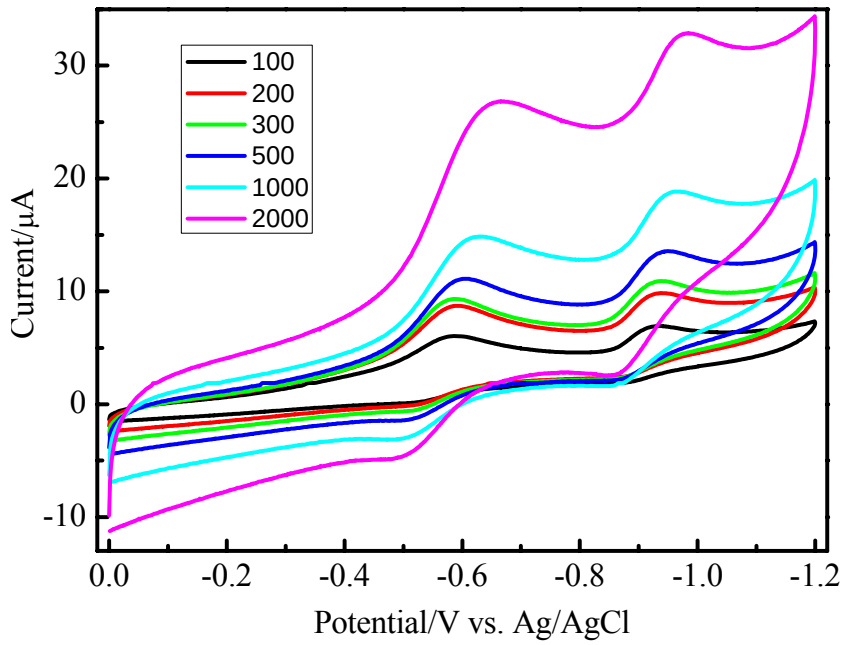


Figure S10. CV curves of **P** in the presence of CF_3COOH as a function of scan rate (100-2000 $mV\cdot s^{-1}$).

References:

1. L. L. Zhu, X. Li, F. Y. Ji, X. Ma, Q. C. Wang and H. Tian, *Langmuir*, 2009, **25**, 3482.
2. D. S. Guo, S. Chen, H. Q. Zhang and Y. Liu, *Chem. Commun.*, 2010, **46**, 2620.