Electronic Supplementary Material (ESI) for Analyst.

# Supporting Information

## The Amplified Electrochemiluminescence Signals Promoted by AIE-Active Moiety of D-A Type Polymer Dots for Biosensing

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## 1. Experimental section

### Materials and Reagents

Tetrahydrofuran (THF) was distilled from sodium in the presence of benzophenone. Poly(styrene-co-maleic anhydride) (PSMA) (average Mn: 1700), tri-n-propylamine (TPrA), $H_2O_2$, $Na_2S_2O_8$, $K_2C_2O_4$, catechol, dopamine and epinephrine were purchased from Sigma-Aldrich Co., Ltd. (Shanghai, China). All other reagents were of analytical grade and used as received. Ultrapure water obtained from a Millipore water purification system ($\geq$ 18 MΩ cm$^{-1}$, Milli-Q, Millipore) was used in all assays. The ECL measurements were conducted in 0.1 M pH 7.4 PBS containing 0.1 M $KNO_3$ as the electrolyte.

### Apparatus

Morphological studies were carried out with JEM-100S transmission electron microscopy (TEM). UV-*vis* absorption spectra were obtained using a Nanodrop-2000C UV-vis spectrophotometer (Thermo, USA). Fluorescence measurements were conducted on a F-7000 fluorescence spectrometer (Hitachi Co., Japan) equipped with a xenon lamp. Electrochemical experiments were performed on a CHI 660B electrochemical workstation (CH Instruments Inc., USA). ECL experiments were carried out on a MPI-E multifunctional electrochemical and chemiluminescent analytical system (Xi'an Remex Analytical Instrument Co., Ltd., China) with a self-made electrochemical cell. The ECL spectra were recorded on a CHI 660B electrochemical workstation in conjunction with a Hitachi F-7000 fluorescence spectrometer using luminescence mode under the closed shutter. NMR spectra were obtained from Bruker Avance 400 spectrometer with 400 MHz for $^1$H NMR, 100 MHz, 376 MHz for $^{19}$F NMR and reported as parts per million (ppm) from tetramethyl silane (TMS) as internal standard. Molecular weight was determined by gel permeation chromatography (GPC) with a Waters 244 HPLC pump, and THF was used as solvent relative to polystyrene standard.

**Synthesis of P-1, P-2, P-3 and mode polymer**

**Table S1. Yields and GPC data**

| | Yield | $M_w$ | $M_n$ | PDI |
|---|---|---|---|---|
| **P-1** | 88.2% | 13040 | 8390 | 1.55 |
| **P-2** | 60.7% | 9400 | 7650 | 1.23 |
| **P-3** | 54.3% | 7670 | 5570 | 1.38 |
| Model Polymer | 57.0% | 7650 | 6880 | 1.11 |

Synthesis of **M-3**: To a solution of **7** (1.30 g, 7.38 mmol) in ethyl acetate (15 mL), $B_2O_3$ (0.25 g, 3.69 mmol) and **8** (2.74 g, 14.78 mmol) was added and stirred under 60°C for 30 min. Then $B(OBu\text{-}n)_3$ (3.38 g, 14.78 mmol) in 10 mL was added and stirred under 60°C for another 30 min. After $n$-$BuNH_2$ (0.21 g, 2.95 mmol) was added, the mixture was refluxed overnight and filtered to give a raw product **9** as a yellow solid. The raw product was solved in 100 mL $CH_2Cl_2$ without purify and $BF_3\cdot Et_2O$ (1.50 g, 10.54 mmol) was added. After the mixture was refluxed overnight, the solvent was removed and the mixture was purified with silica gel column ($CH_2Cl_2$ : petroleum ether = 1 : 2, v/v) to give the **M-3** as an orange solid (1.66 g, 40.4%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$: 8.020 (d, $J$ = 15.5 Hz, 2H), 7.565-7.549 (m, 3H), 7.494-7.473 (d, $J$ = 8.5 Hz, 4H), 7.321-7.298 (m, 2H), 7.260 (d, $J$ = 8.5 Hz, 4H), 6.510 (d, $J$

= 15.5 Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$) *δ*: 178.42, 146.56, 133.08, 132.45, 131.88, 130.50, 129.37, 129.21, 126.53, 119.81. $^{19}F$ NMR (376 MHz, $CDCl_3$) *δ*: -140.15.

Synthesis of model polymer: **M-1** (0.200 g, 0.380 mmol), **M-2** (0.190 g, 0.380 mmol), $Pd(PPh_3)_4$ (0.050 g, 5% e. q.) and $K_2CO_3$ (4.56 g, 33.043 mmol) were dissolved in 23 mL toluene and 15 mL water. The reaction was processed through the method of **P-1** and gave model polymer as a brown solid (0.131 g, 57.0%). $^1H$ NMR (400 MHz, $CDCl_3$) *δ* 8.42-8.08 (m, 2H), 7.73-7.61 (m, 2H), 7.54-7.34 (m, 6H), 7.54-7.36 (m, 14H), 4.30-4.27 (m, 2H), 1.86-1.85 (m, 1H), 1.61 (s, 2H), 1.32-1.24 (m, 10H), 0.88-0.82 (m, 2H). GPC data: $M_w = 7650$, $M_n = 6880$, PDI = 1.11.

Synthesis of **P-1**: **M-1** (0.120 g, 0.230 mmol), **M-2** (0.100 g, 0.219 mmol), **M-3** (0.007 g, 0.011 mmol) and $Pd(PPh_3)_4$ (0.028 g, 5% e.q.) were dissolved in 14 mL toluene and 9 mL $K_2CO_3$ aqueous solution (2 M) was added. The mixture was stirred for 48 h under 75 $^oC$ in Ar atmosphere. The reaction mixture was then cooled to room temperature and the organic layer was separated out. After the solvent was removed, the mixture was dissolved in 1 mL $CH_2Cl_2$, added in 300 mL $CH_3OH$ and stirred for another 30 min. The mixture was filtered and gave **P-1** as a brown solid (0.080 g, 58.0%). $^1H$ NMR (400 MHz, $CDCl_3$) *δ* 7.73-7.67 (m, 2H), 7.49-7.39 (m, 6H), 7.25-7.10 (m, 16H), 4.32-4.28 (m, 2H), 1.88-1.87 (m, 1H), 1.33-1.24 (m, 12H), 0.86-0.84 (m, 2H). GPC data: $M_w = 13040$, $M_n = 8390$, PDI = 1.55.

Synthesis of **P-2**: **M-1** (0.120 g, 0.230 mmol), **M-2** (0.095 g, 0.208 mmol), **M-3** (0.014 g, 0.022 mmol) and $Pd(PPh_3)_4$ (0.028 g, 5% e.q.) were dissolved in 14 mL toluene and 9 mL $K_2CO_3$ aqueous solution (2 M) was added. The reaction was processed with the method of **P-1** and gave **P-2** as a brown solid (0.085 g, 60.7%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.68-7.65 (m, 2H), 7.51-7.41 (m, 7H), 7.22-7.10 (m, 13H), 4.27 (s, 2H), 1.85 (s, 2H), 1.31-1.23 (m, 12H), 0.86-0.84 (m, 3H). GPC data: $M_w$ = 9400, $M_n$ = 7650, PDI = 1.23.

Synthesis of **P-3**: **M-1** (0.120 g, 0.230 mmol), **M-2** (0.084 g, 0.186 mmol), **M-3** (0.028 g, 0.044 mmol) and $Pd(PPh_3)_4$ (0.028 g, 5% e.q.) were dissolved in 14 mL toluene and 9 mL $K_2CO_3$ aqueous solution (2 M) was added. The reaction was processed with the method of **P-1** and gave **P-3** as a dark red solid (0.076 g, 54.3%). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.73-7.66 (m, 2H), 7.51-7.40 (m, 6H), 7.15-7.04 (m, 16H), 4.31 (s, 2H), 1.26 (s, 12H), 0.87-0.84 (m, 3H). GPC data: $M_w$ = 7670, $M_n$ = 5570, PDI = 1.38.

## 2. Supplementary Figures

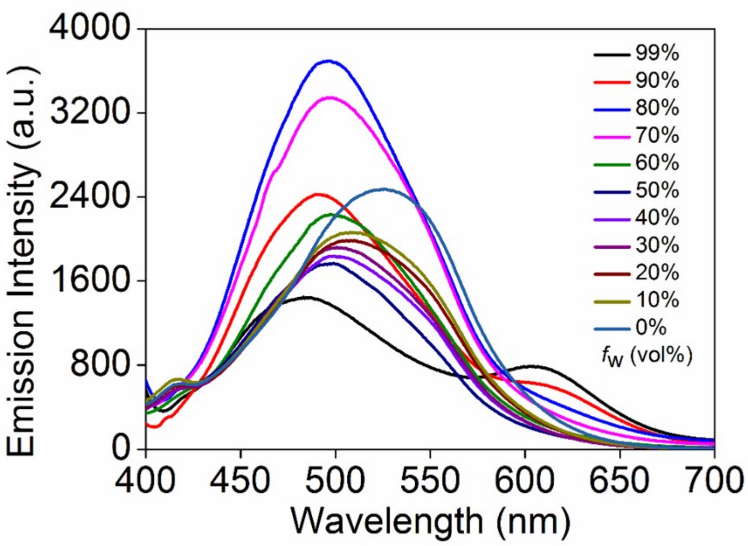


**Fig. S1** The Fluorescence spectra of **P-2** ($1\times10^{-5}$ M corresponding to carbazole moiety in THF-$H_2O$ mixtures, $\lambda_{ex}$ = 370 nm)

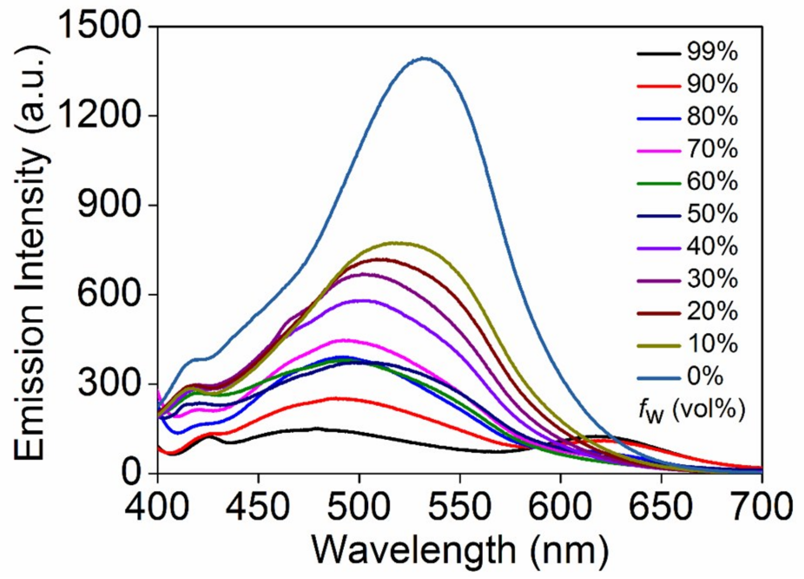


**Fig. S2** The Fluorescence spectra of **P-3** (1×$10^{-5}$ M corresponding to carbazole moiety in THF-$H_2O$ mixtures, $\lambda_{ex}$ = 370 nm)

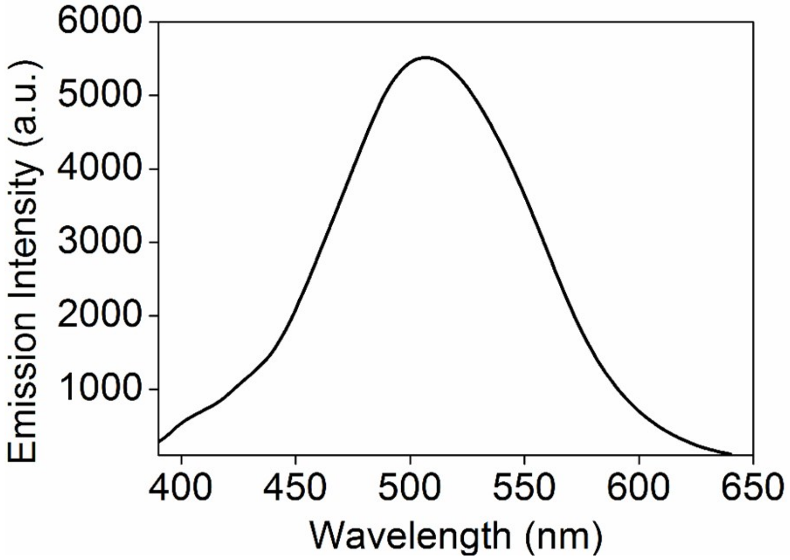


**Fig. S3** The fluorescence spectra of model polymer in THF (1×$10^{-5}$ M corresponding to carbazole moiety in THF, $\lambda_{ex}$ = 370 nm)

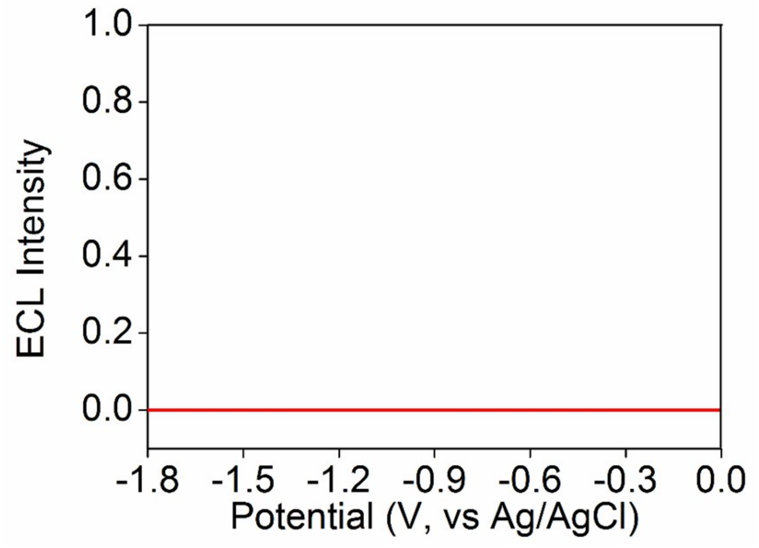


**Fig. S4** ECL–potential curves of **P-1** to **P-3** Pdots in 0.1 M PBS (pH = 7.4) containing 0.1 M $KNO_3$ and 25 mM $H_2O_2$ or $Na_2S_2O_8$ (PMT set at 400 V).

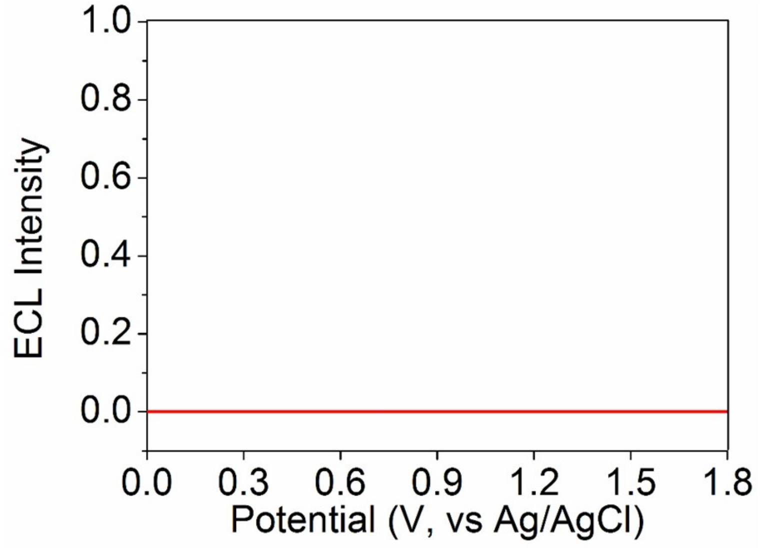


**Fig. S5** ECL–potential curves of **P-1** to **P-3** Pdots in 0.1 M PBS (pH = 7.4) containing 0.1 M $KNO_3$ and 25 mM $K_2C_2O_4$ (PMT set at 400 V).

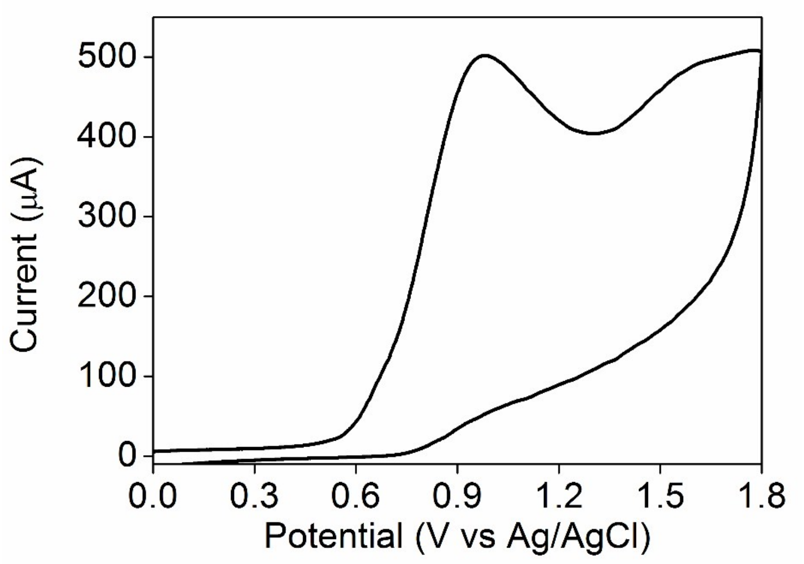


**Fig. S6** CV of bare GCE in 0.1 M pH 7.4 PBS in the presence of 0.1 M TPrA as anodic co-reactant. Scan rate: 100 mV s$^{-1}$.

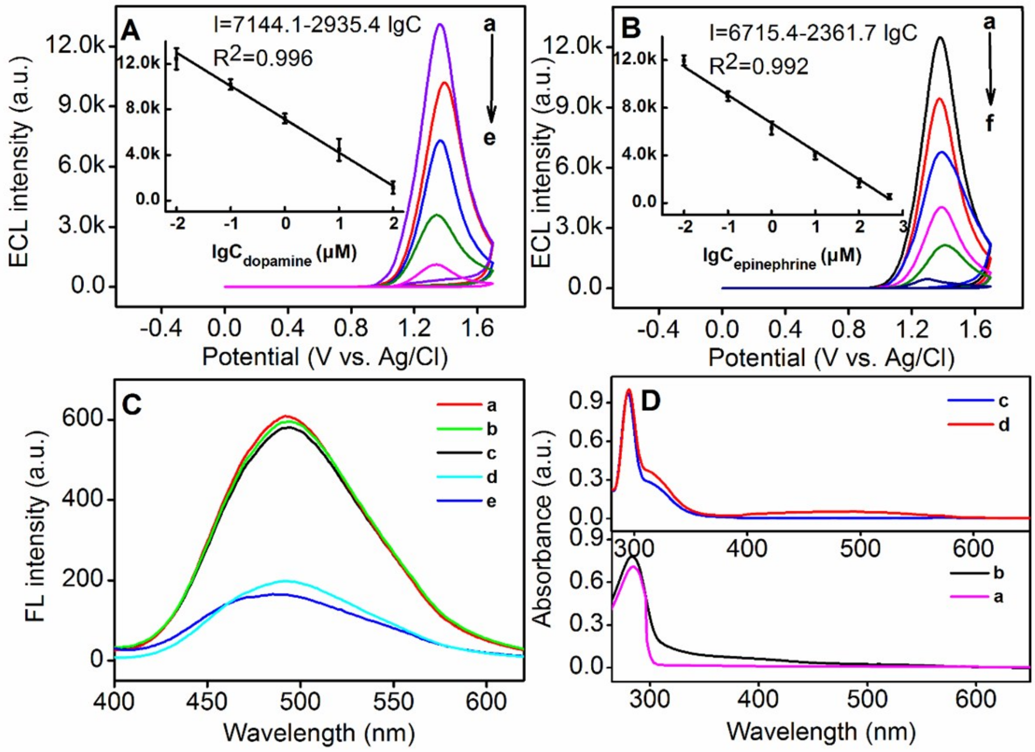


**Fig. S7.** (A) ECL–potential curves of Pdots in the presence of 0.01, 0.1, 1, 10, 100 and 500 μM epinephrine (a to f) Inset: plot of ECL intensity vs. logarithm value of epinephrine concentration. (PMT set at 500 V) (B) ECL–potential curves of Pdots in the presence of 0.01, 0.1, 1, 10, 100 μM dopamine (a to e) Inset: plot of ECL intensity vs. logarithm value of dopamine concentration. (PMT set at 500 V) (C) FL spectra of Pdots in (a) absence and (b−d) presence of 100 μM epinephrine (b) or dopamine(c), and 100 μM oxidized epinephrine (d) or oxidized dopamine (e). (D) UV−vis absorption spectra of epinephrine (a) and oxidized epinephrine (b), dopamine (c) and oxidized dopamine(d).

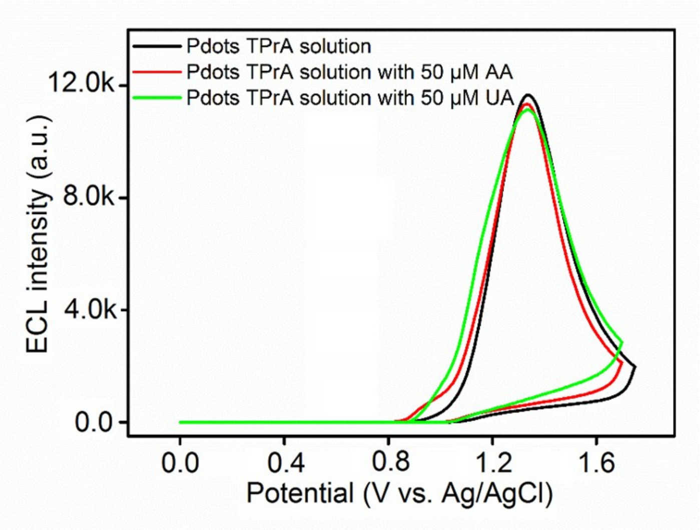
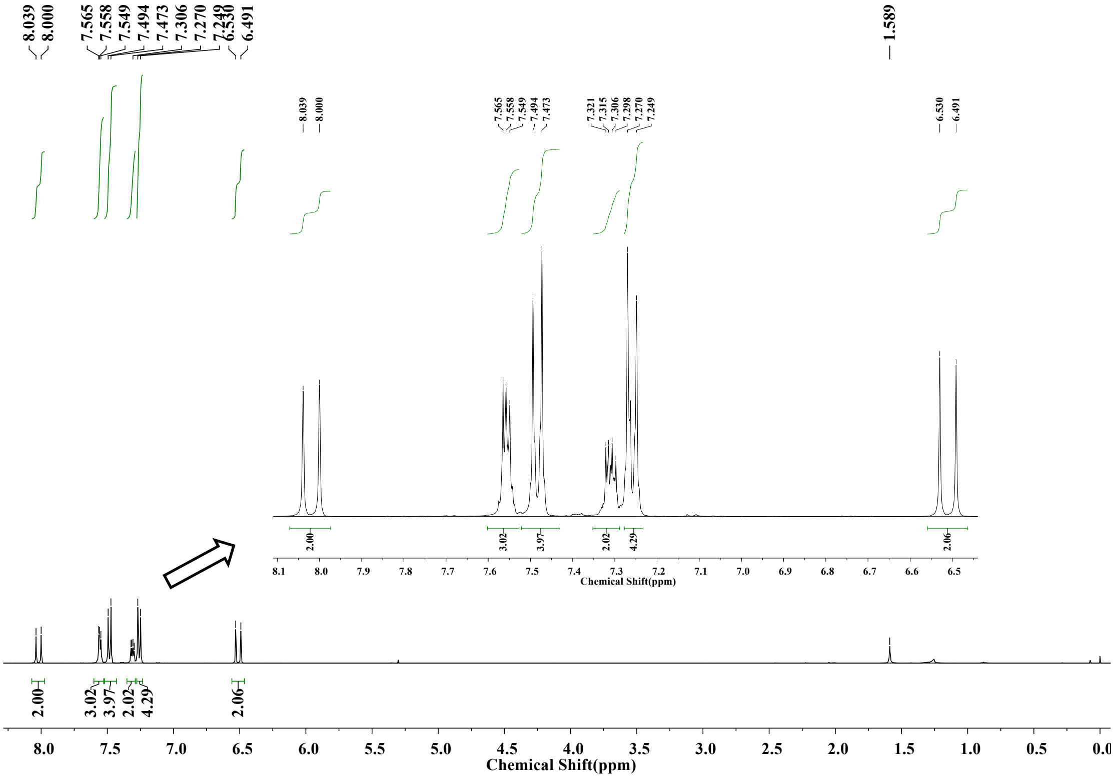


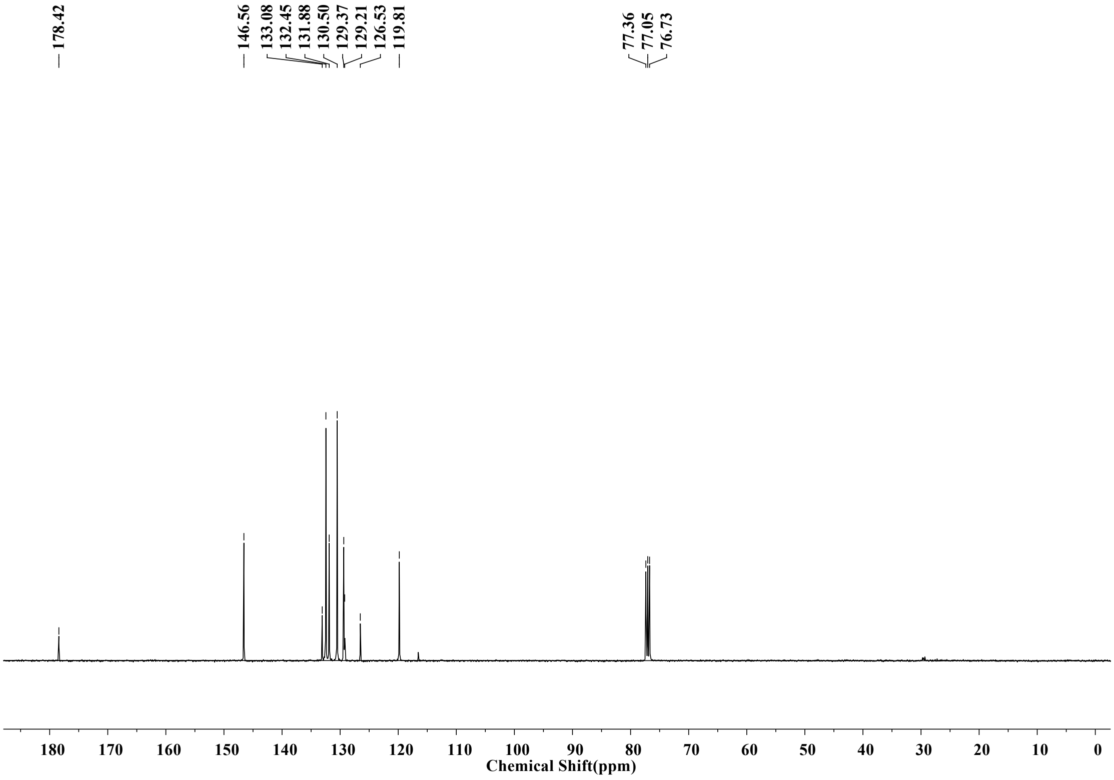
**Fig. S8.** ECL–potential curves of 0.1 M pH 7.4 PBS containing 25 μg mL $^{-1}$ Pdots and 25mM TPrA in absence (black curve) and presence of 50 μM AA (red curve) and UA (green curve). (PMT set at 500 V)

## 3. NMR Spectra

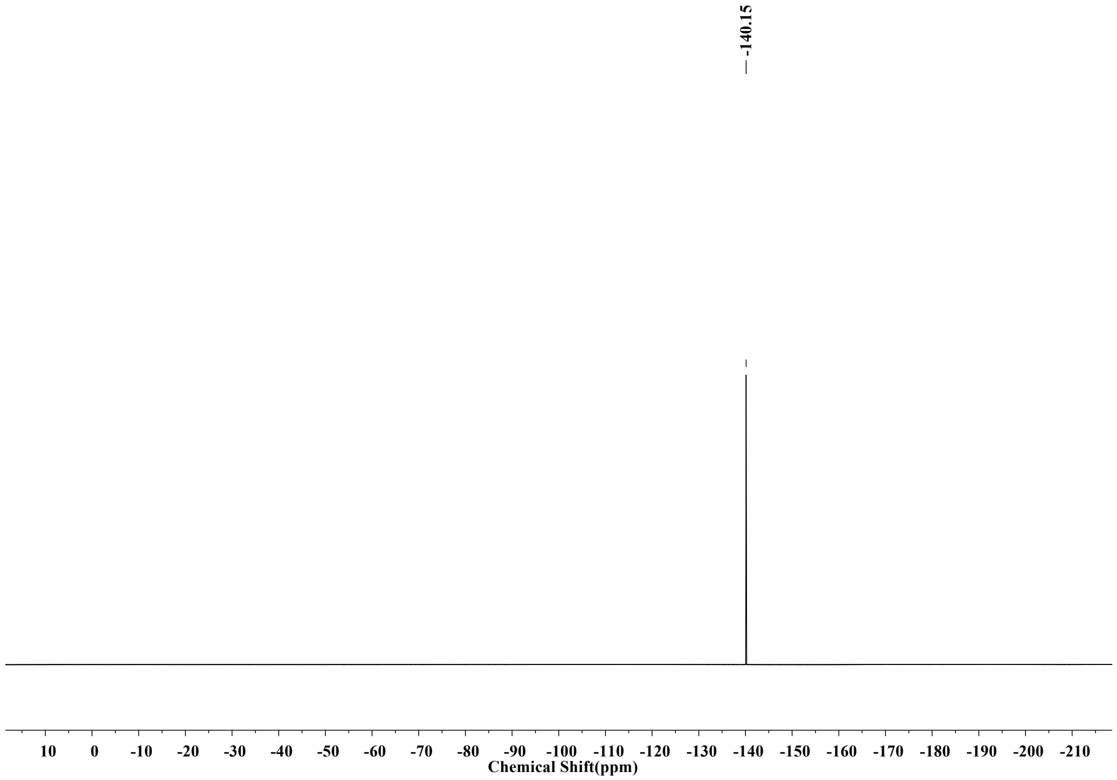
$^1$H NMR of **M-3**



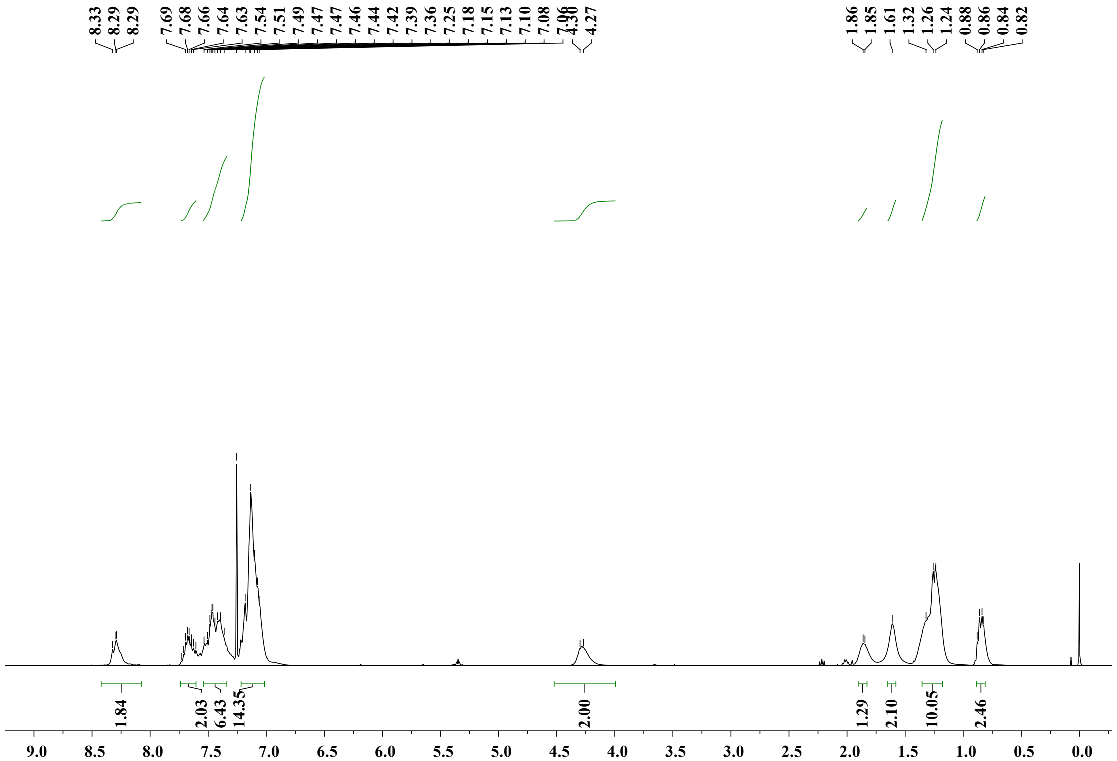
$^{13}$C NMR of **M-3**



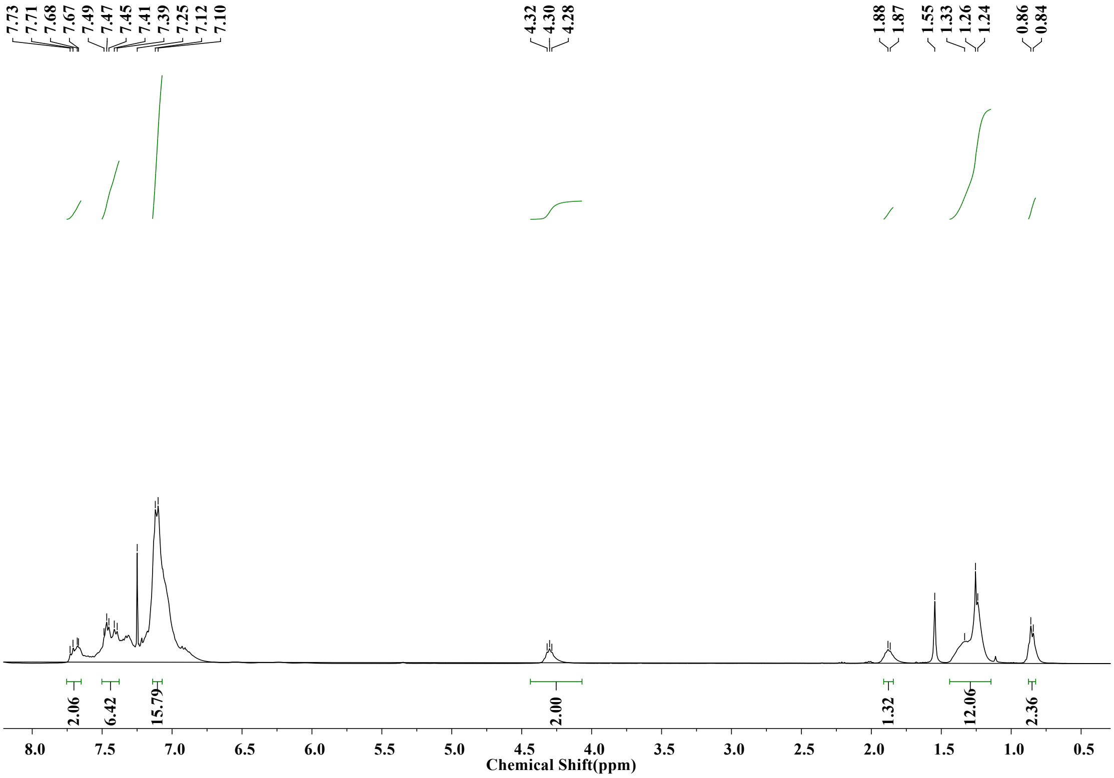
$^{19}$F NMR of **M-3**



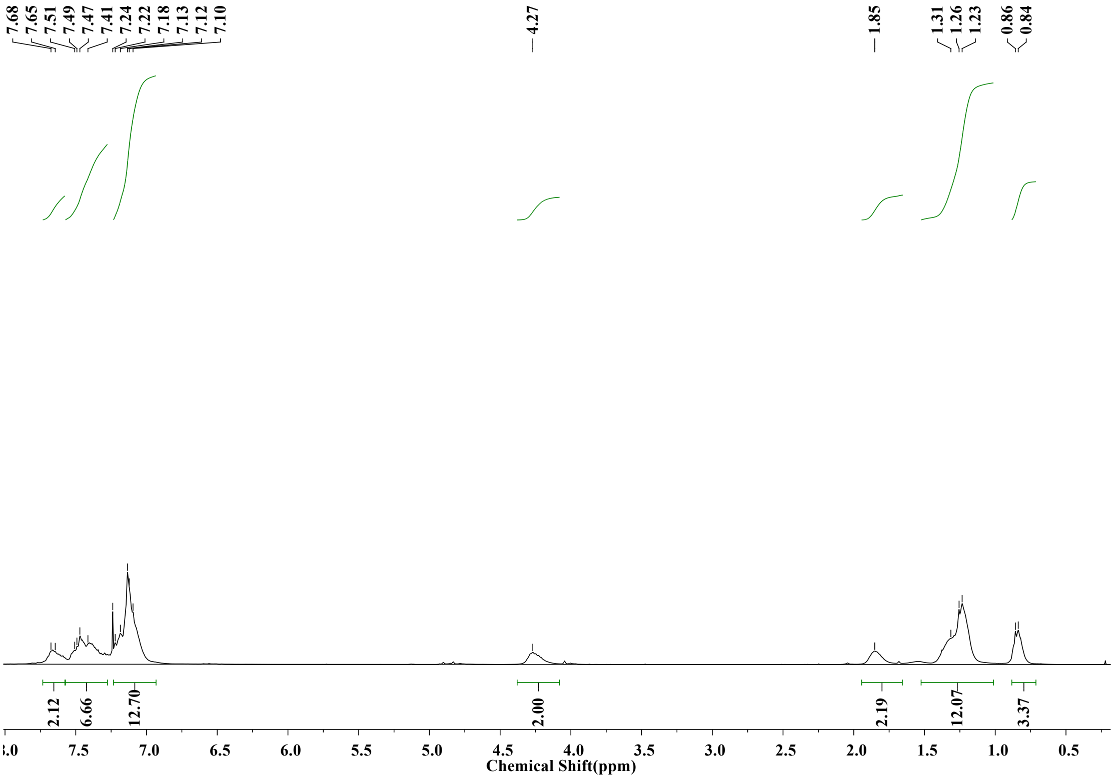
$^{1}$H NMR of model polymer



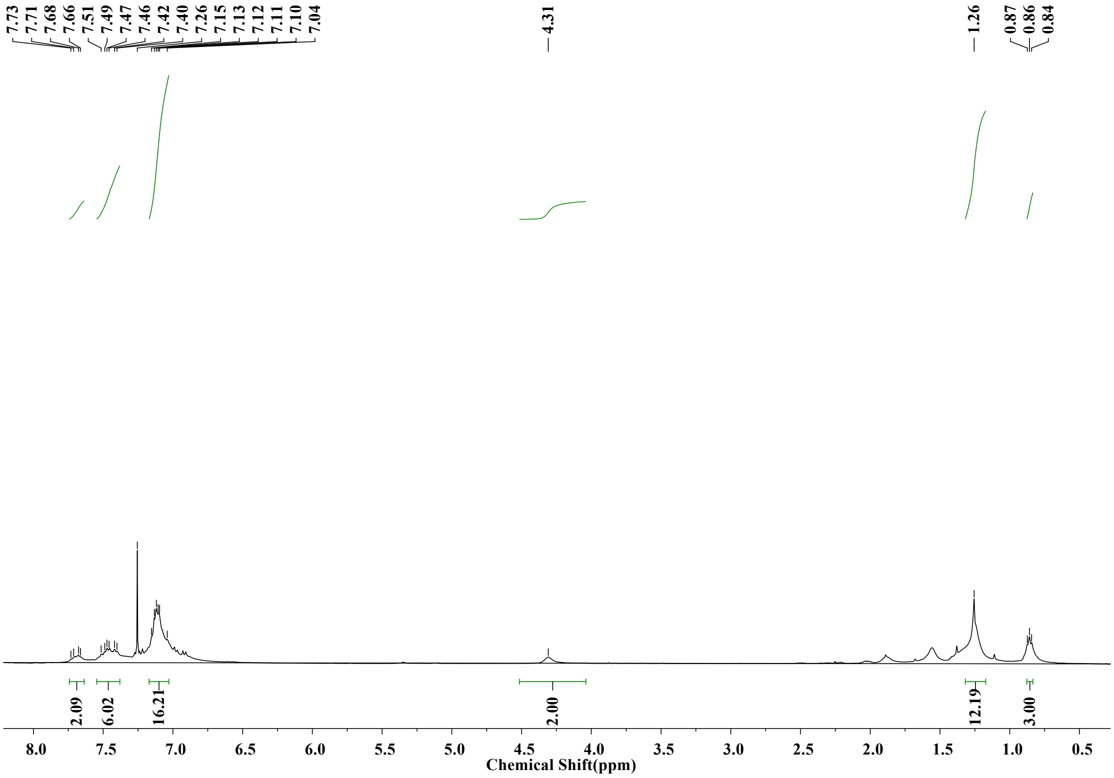
$^1$H NMR of **P-1**



$^1$H NMR of **P-2**



$^1$H NMR of **P-3**


7.73
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7.66
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7.49
7.47
7.46
7.42
7.40
7.26
7.15
7.13
7.12
7.11
7.10
7.04
4.31
1.26
0.87
0.86
0.84
2.09
6.02
16.21
2.00
12.19
3.00
8.0
7.5
7.0
6.5
6.0
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