

Supporting information

Proton-responsive azulene-based conjugated polymer with nonvolatile memory effects

Zhizheng Zhao^a, Weiwei Huan^{b,*}, Chen Sun^a, Mohamed E. El-Khouly^c, Bin Zhang^{a,*}, and Yu Chen^{a,*}

^a Key Laboratory for Advanced Materials and Joint International Research Laboratory of Precision Chemistry and Molecular Engineering, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai, China.

^b Zhejiang Provincial Key Laboratory of Chemical Utilization of Forestry Biomass, College of Chemistry and Materials Engineering, Zhejiang A&F University, Hangzhou, Zhejiang 311300, China.

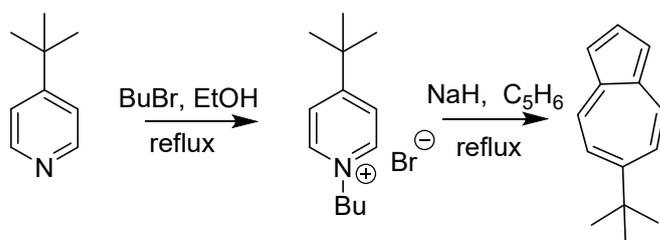
^c Institute of Basic and Applied Sciences, Egypt-Japan University of Science and Technology (E-JUST), Alexandria, Egypt.

Experimental

Reagents

Unless otherwise noted, all chemicals were purchased from Adamas and used without further purification. Organic solvents were purified, dried, and distilled under dry argon. All reactions were performed under an argon atmosphere by standard Schlenk techniques.

Synthesis of 6-*tert*-butylazulene (M1)

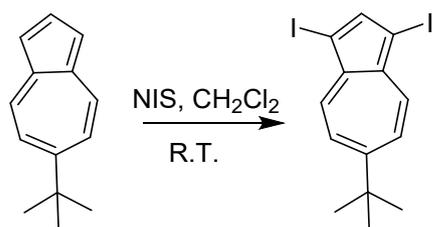


NaH (60% dispersion in mineral oil; 2.0 g, 50 mmol) and DMF (60 mL) were mixed in a three-necked flask, and the mixture was bubbled with nitrogen for 30 min

and cooled to 0 °C. Freshly-cracked C₅H₆ (5 mL, 60 mmol) was added dropwise within 20 min, and the mixture was stirred for another 10 min. 4-(*tert*-butyl)-1-butylpyridinium bromide (14.5 g; 50 mmol) was added, and the solution was allowed to stir at room temperature for 1 h and then heated to reflux for 3 h. The mixture was cooled and extracted repeatedly with hexanes for at least three times. The extracts were combined and evaporated under reduced pressure. The residue was purified via silica column chromatography by eluting with 10% DCM in PE. The blue product fraction was evaporated to give 6-*tert*-butylazulene (M1) (5.32 g, 66% yield). Recrystallization from methanol produced blue crystals.

¹H NMR (CDCl₃, ppm): 1.45 (9H, s), 7.32 (2H, d), 7.35 (2H, d), 7.82 (1H, t), 8.31 (2H, d); ¹³C NMR (CDCl₃, ppm): 31.9, 38.5, 117.3, 120.9, 135.6, 136.0, 138.9, 161.0.

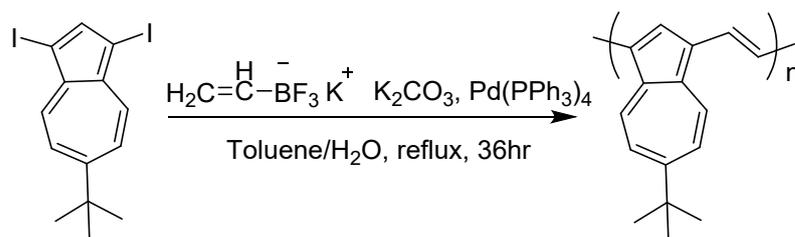
Synthesis of 6-*tert*-butyl-1,3-diiodoazulene (M2)



N-Iodosuccinimide (NIS) (4.5 g, 20 mmol) was added to a solution (0 °C) of 6-*tert*-butylazulene (1.84 g, 10 mmol) in CH₂Cl₂ (100 mL), and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was then filtered through a short alumina column. The solvent was removed *in vacuo* to obtain 6-*tert*-butyl-1,3-diiodoazulene as dark blue crystals without further purification (3.91 g, 90% yield).

¹H NMR (CDCl₃, ppm): 1.46 (9H, s), 7.53 (2H, d), 7.90 (1H, s), 8.13 (2H, d); ¹³C NMR (CDCl₃, ppm): 31.7, 38.9, 73.65, 123.1, 137.7, 139.4, 148.1, 163.7.

Synthesis of Poly(azulene vinylene) (PAV)



K_2CO_3 (414 mg, 3 mmol) was dissolved in 18 mL toluene-water (v/v = 2/1) mixed solvent and the solvent was bubbled with nitrogen for 15 min before use. Then 6-*tert*-butyl-1,3-diodoazulene (M2) (436 mg, 1 mmol) and potassium vinyltrifluoroborate (134 mg, 1 mmol) was added to the mixture followed by another nitrogen bubble degassing operation for 15 min. After that, $\text{Pd}(\text{PPh}_3)_4$ (27 mg, 2% mmol) was added. The reaction mixture was then stirred at 100 °C for 36 h. After cooling to room temperature, the mixture was poured slowly into 100 mL of methanol, filtered using a Buchner funnel, the crude product was re-dissolved in CHCl_3 and was quickly passed through a column of siliceous earth to remove the residual catalyst. After removing the solvent, the crude product was subjected to Soxhlet extraction sequentially with acetone and hexane to remove unreacted monomers to obtain dark blue powders (124 mg, 60% yield). GPC (THF): $M_n = 4.41 \times 10^3$; PDI = 1.12.

Device fabrication and characterization

The ITO glass substrate was carefully pre-cleaned sequentially with deionized water, acetone, and 2-propanol in an ultrasonic bath for 15 min, and then treated with oxygen plasma. A PAV solution ($100 \mu\text{L}$, $10 \text{ mg} \cdot \text{mL}^{-1}$) in DMF was spin-coated onto the pre-cleaned ITO sheet at a spinning speed of 1500 rpm for 60 s, followed by removal of the solvent under vacuum at 55 °C overnight. The Al top electrodes were deposited on the surface of the active layer through a shadow mask at 10^{-7} Torr via e-beam evaporation. All electrical measurements were performed on a Keithley 4200 semiconductor parameter analyzer under ambient conditions without any device encapsulation.

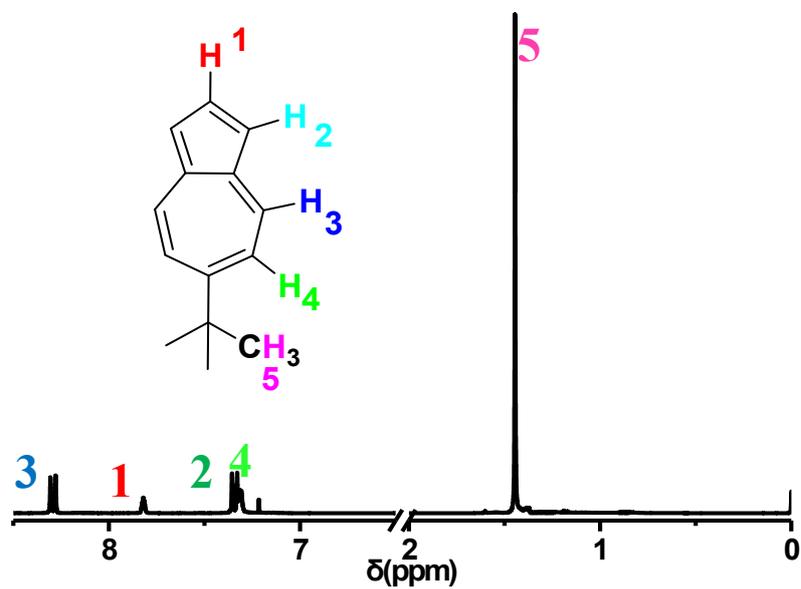


Figure S1 ^1H NMR spectrum of M1.

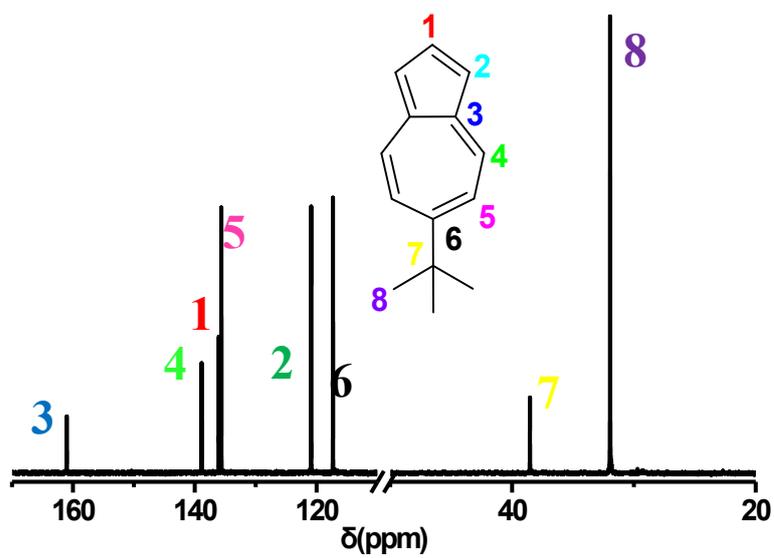


Figure S2 ^{13}C NMR spectrum of M1.

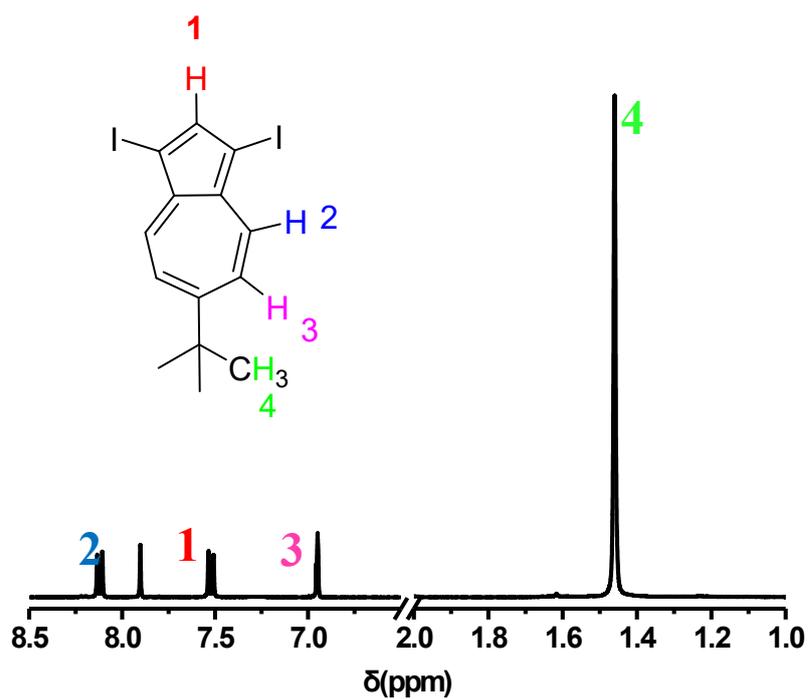


Figure S3 ¹H NMR spectrum of M2.

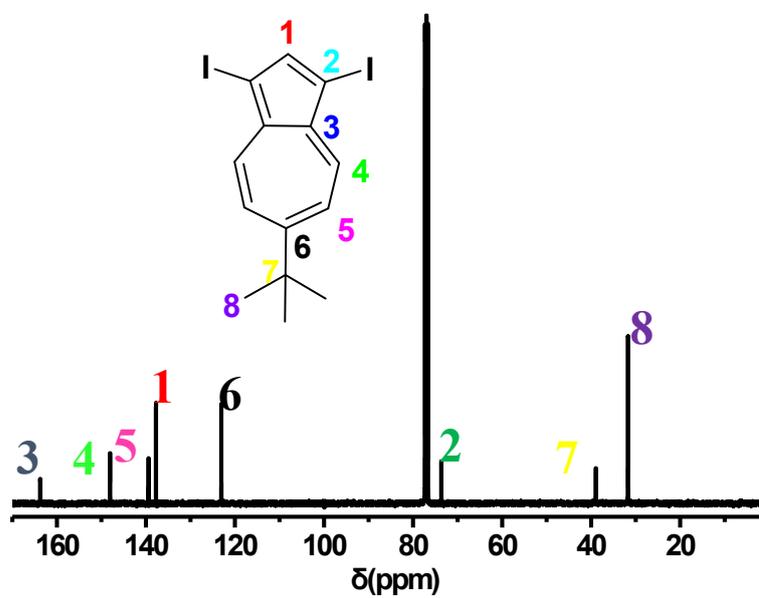


Figure S4 ¹³C NMR spectrum of M2.

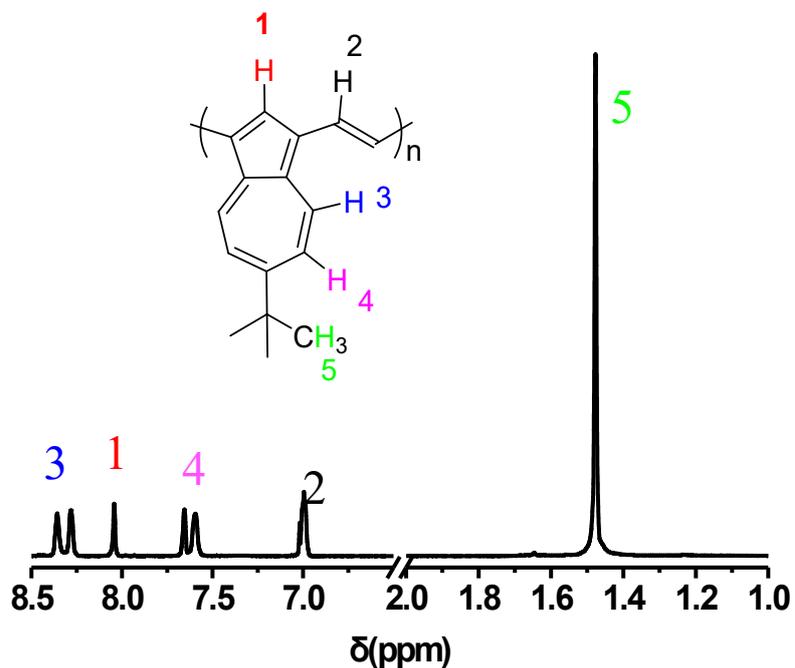


Figure S5 ¹H NMR spectrum of PAV.

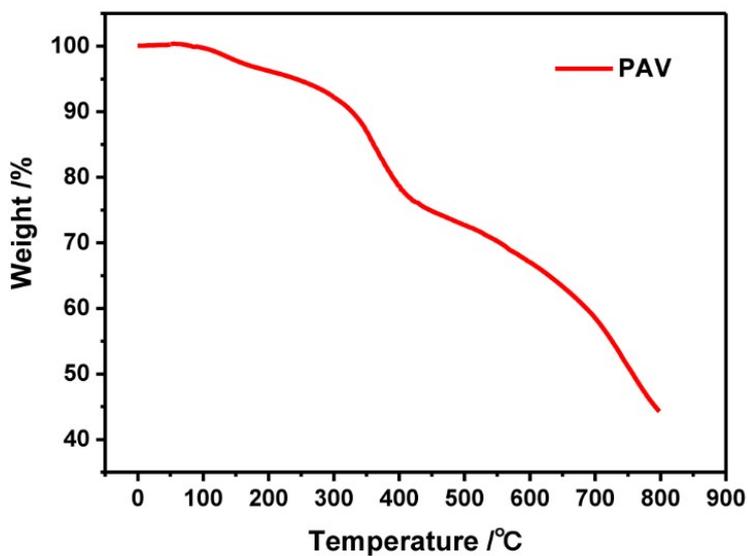


Figure S6. Thermogravimetric curves of PAV measured in flowing N₂.

Figure S6 shows the TGA curves of PAV. The conjugate polymer PAV exhibits good thermal stability with the initial decomposition temperature of 135 °C, while the temperature at 10 % weight loss is ~330 °C.