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Supporting Information

Terminal Amino Monomethylation Triggering Intermolecular H- to J-Aggregations to Realize Tunable Memory Devices

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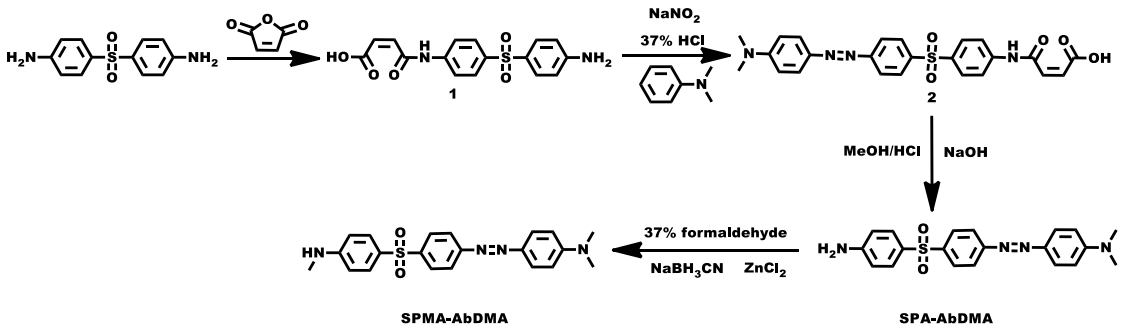
Experimental Procedures

Materials

Hydrochloric acid (37%), Sodium hydroxide (98%), Methanol (99.7%), Ethanol (99.7%), 4,4'-Diaminodiphenylsulfone (97%), N,N-Dimethylformamide (99.8%), Sodium nitrite (99%), N,N-Dimethylaniline (99.5%) and Maleic anhydride (99%) were purchansed from (Sinopharm Chemical Reagent Co. Ltd., China); Sodium cyanoborohydride (95%) was purchased from commercial sources (Alfa Aesar). All other reagents are used as received unless further instruction.

Preparation of SPA-AbDMA and SPMA-AbDMA

SPA-AbDMA was synthesized in three steps: first, one amino of 4,4'-sulfonyldianiline was protected by reacting with maleic anhydride in acetone to afford 4-((4-((4-aminophenyl)sulfonyl)phenyl)amino)-4-oxobut-2-enoic acid (2) in 70% yield. Then this product was transformed into diazonium salt in ice bath before reacting with N,N'-dimethylaniline to give the protected intermediate in 68% yield. Finally, SPA-AbDMA was obtained after deprotection of the amino in 55% yield. SPMA-AbDMA was synthesized through further monomethylation at the terminal amino of SPA-AbDMA in 64% yield.



Scheme S1. Synthetic route of **SPA-AbDMA** and **SPMA-AbDMA**.

4-((4-((4-aminophenyl)sulfonyl)phenyl)amino)-4-oxobut-2-enoic acid (1)

A solution of 4,4'-sulfonyldianiline (2.48 g, 10.0 mmol) in acetone (20.0 mL) was prepared. To this solution, maleic anhydride (0.98 g, 10.0 mmol) in 5.0 mL acetone was added slowly. White precipitate was formed and stirred continuously for 8 hours. The slurry was filtered and washed with ice cold acetone to remove the acetone soluble materials and dried. The yield was 70%. ^{1}H NMR (DMSO-d6, 400MHz), δ (ppm): 12.88 (s, 1H), 10.71-10.65 (d, 1H), 7.89-7.87 (d, 1H), 7.82-7.75 (m, 4H), 7.52-7.50 (d, 2H), 6.61-6.59 (d, 2H), 6.50-6.45 (d, 1H), 6.33-6.30 (d, 1H), 6.14 (s, 2H).

(Z)-4-((4-((4-((E)-(4-(dimethylamino)phenyl)diazenyl)phenyl)sulfonyl)phenyl)amino)-4-oxobut-2-enoic acid (2)

A mixture of compound **1** (3.44 g, 10.0 mmol), DMF (40.0 mL), and concentrated chlorhydric acid (12.0 mL) was added dropwise to the solution of sodium nitrite (0.69 g, 10.0 mmol) in DMF (10 mL) at 0-5 ^{o}C over 60 minutes. After the solution had become transparent, the mixture was filtered and the filtrate (azonium salt solution) was kept in the ice bath. N,N-dimethylaniline (1.21 g, 10.0 mmol) was dissolved in 10 mL DMF and was added slowly into the azonium salt solution, the mixture was stirred in the ice bath for 1 hour and the pH value was neutralized to 6-7, then kept stirring for another 3 hours the solution was filtered and the crude product was recrystallized from ethanol (yield 68%).

(E)-4-((4-((4-aminophenyl)sulfonyl)phenyl)diazenyl)-N,N-dimethylaniline (SPA-AbDMA)

A mixture of compound **2** (1.0 g, 2.1 mmol), methanol (50.0 mL), and concentrated chlorhydric acid (50.0 mL) was refluxed over 1 hour, and the solution was filtered at high temperature. NaOH (12%) was used to neutralize the pH value until red precipitate was formed. Then the methanol was evaporated and the crude product was dropped into the ice cold water. The solution was filtered to get the solid crude product. The crude product was purified by column chromatography on a silica gel (ethyl acetate/chloroform, 1:5). The yield was 55%. ^{1}H NMR (DMSO, 400MHz), δ (ppm): 7.95-7.93 (d,2H), 7.87-7.85 (d,2H), 7.82-7.79 (d,2H), 7.58-7.56 (d,2H), 6.85-6.83 (d,2H), 6.64-6.62 (d,2H),

6.23 (s,2H), 3.08 (s,6H). ^{13}C NMR (151 MHz, dmso) δ 154.98, 154.17, 153.57, 143.33, 143.04, 129.94, 128.24, 125.88, 125.60, 122.84, 113.50, 112.01, 40.54 – 39.44. HRMS m/z: [M+H]+ calcd for C20H20N4O2S, 380.1307; found, 380.1306.

(E)-N,N-dimethyl-4-((4-((4-(methylamino)phenyl)sulfonyl)phenyl)diazenyl)aniline (SPMA-AbDMA)

To a stirred solution of SPA-AbDMA (0.19 g, 0.5 mmol) and formaldehyde (37%, 0.125 ml, 1.56 mmol) in anhydrous THF (25.0 mL), a solution of sodium cyanoborohydride (0.0315 g, 0.5 mmol) and zinc chloride (0.034 g, 0.25 mmol) in THF (4.0 mL) was added at ambient temperature under nitrogen atmosphere. The reaction mixture was stirred at ambient temperature for 2 h and then quenched with aqueous NaOH [2 N]. The biphasic mixture was extracted with dichloromethane (3 10 mL) and the combined organic extracts were washed with water (10 mL), brine (10 mL), dried over sodium sulfate, and evaporated to dryness under reduced pressure. The residue was subjected to silica column chromatography on a silica gel (ethyl acetate/chloroform, 1:7) to afford pure compound. The yield was 64%. ^{1}H NMR (DMSO, 400MHz), δ (ppm): 7.96-7.94 (d,2H), 7.87-7.85 (d,2H), 7.82-7.79 (d,2H), 7.65-7.63 (d,2h), 6.85-6.83 (d,2H), 6.79-6.78 (m,1H), 6.64-6.61 (d,2H), 3.08 (s,6H), 2.71-2.70 (d,3H). ^{13}C NMR (151 MHz, dmso) δ 154.98, 154.15, 153.57, 143.34, 143.04, 129.79, 128.22, 125.88, 125.49, 122.84, 112.01, 111.59, 40.54 – 39.44, 29.51. HRMS m/z: [M+H]+ calcd for C21H22N4O2S, 394.1463; found, 394.1466.

Memory Device Fabrication

The memory device was fabricated on the indium-tin oxide (ITO)-coated glass, with the configuration of ITO/small molecules/Al. Before the fabrication of the organic layer, the ITO glass was pre-cleaned with deionized water, acetone, and alcohol, in that order, in an ultrasonic bath for 20 min, respectively. A 15 mg SPA-AbDMA/SPMA-AbDMA molecules were placed into a evaporation baot in a vacuum deposition equipment. Then, the molecule was thermally deposited to the ITO glass slowly until the vacuum reaching to 10^{-5} Pa. Subsequently, a layer of Al, about 100 nm in thickness and 0.5 mm in diameter, was thermally evaporated and deposited onto the organic film surface at about 10^{-6} Torr through a shadow mask to form the top electrode.

Measurements

All electrical measurements of the device were characterized under ambient conditions, without any encapsulation, using a Agilent B1500A semiconductor parameter analyzer equipped with HP 8110A pulse generator. NMR spectra were obtained on an Inova 400 MHz FT-NMR spectrometer. UV-vis absorption spectra were carried out at room temperature from 250 to 600 nm with a Shimidazu UV-3600 spectrophotometer. Thermo gravimetric analysis (TGA) was conducted on a TA instrument Dynamic TGA 2950 at a heating rate of 10 ^{o}C·min^{-1} under a nitrogen flow rate of 50 mL min^{-1}. Atomic force microscopy (AFM) measurements were performed by using a MFP-3DTM (Digital Instruments/Asylum Research) AFM instrument in tapping mode. Cyclic voltammetry was performed at room temperature using an ITO working electrode, a reference electrode Ag/AgCl and a counter electrode (Pt wire) at a sweep rate of 0.1 V/s (CorrTest CS Electrochemical Workstation analyzer). A 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in anhydrous acetonitrile was used as an electrolyte. X-ray diffraction (XRD) analysis was performed on film using a Shimadzu XRD-6000 spectrometer with a Cu KR monochromatic radiation sourceat 40 kV and 30 mA.

Results and Discussion

^{1}H NMR

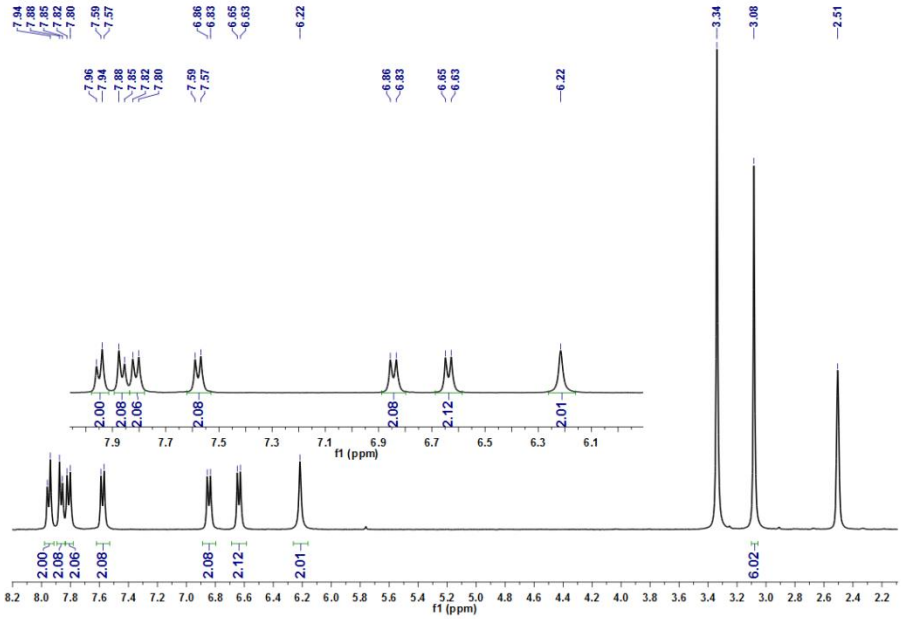


Figure S1-1. ^{1}H NMR spectra of **SPA-AbDMA**.

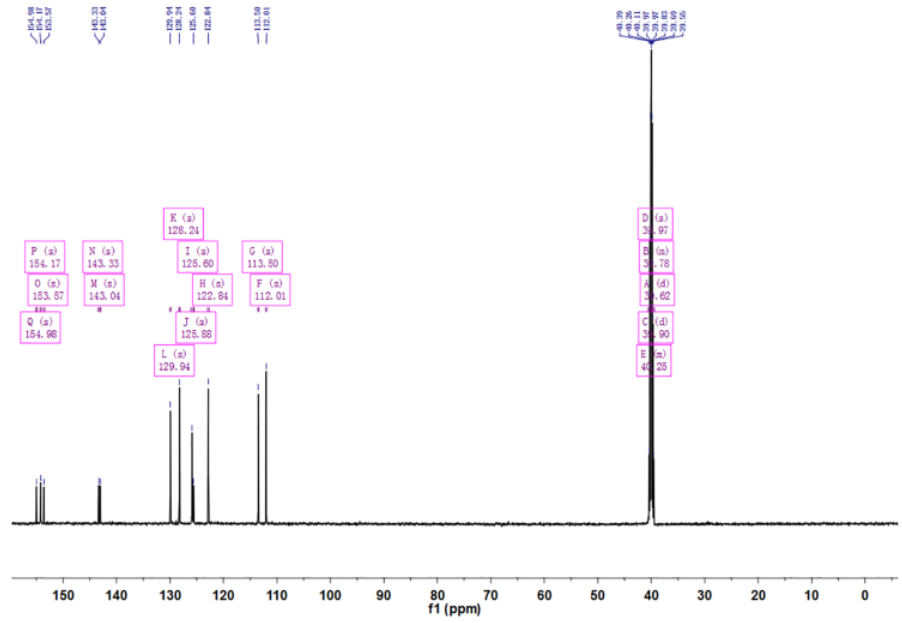


Figure S1-2. ^{13}C NMR spectra of **SPA-AbDMA**.

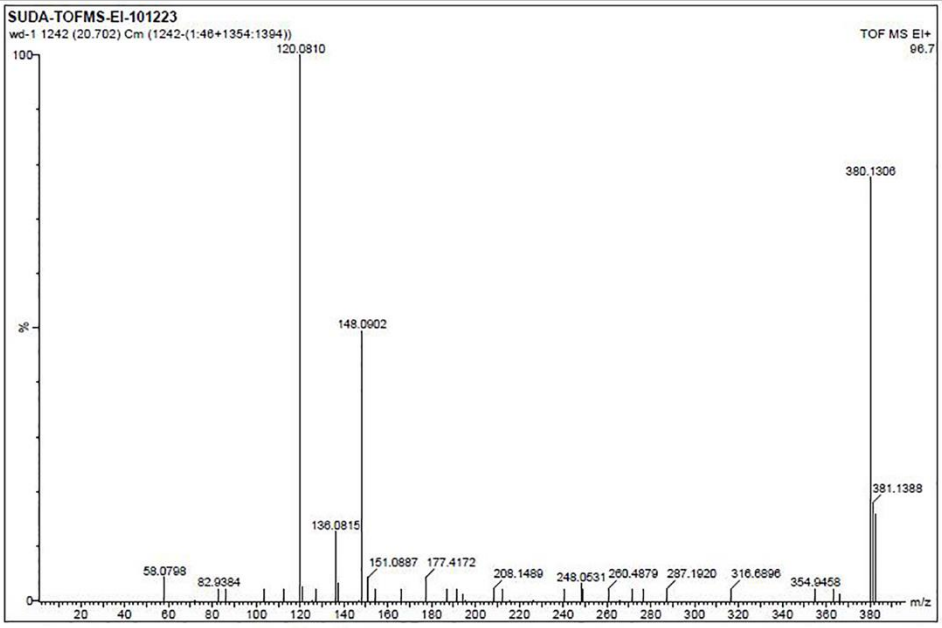


Figure S1-3. HRMS spectra of **SPA-AbDMA**.

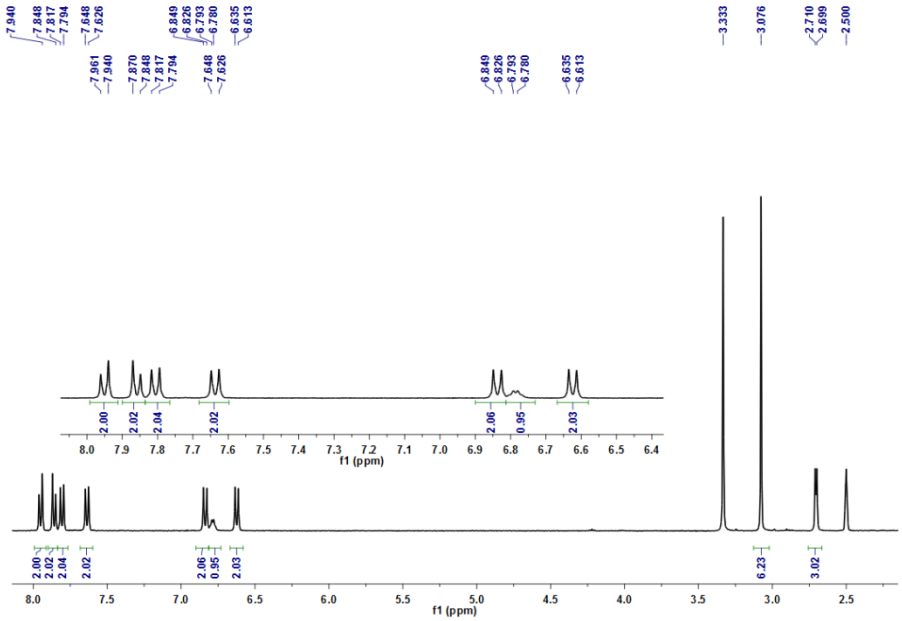


Figure S2-1. [1]H NMR spectra of **SPMA-AbDMA**.

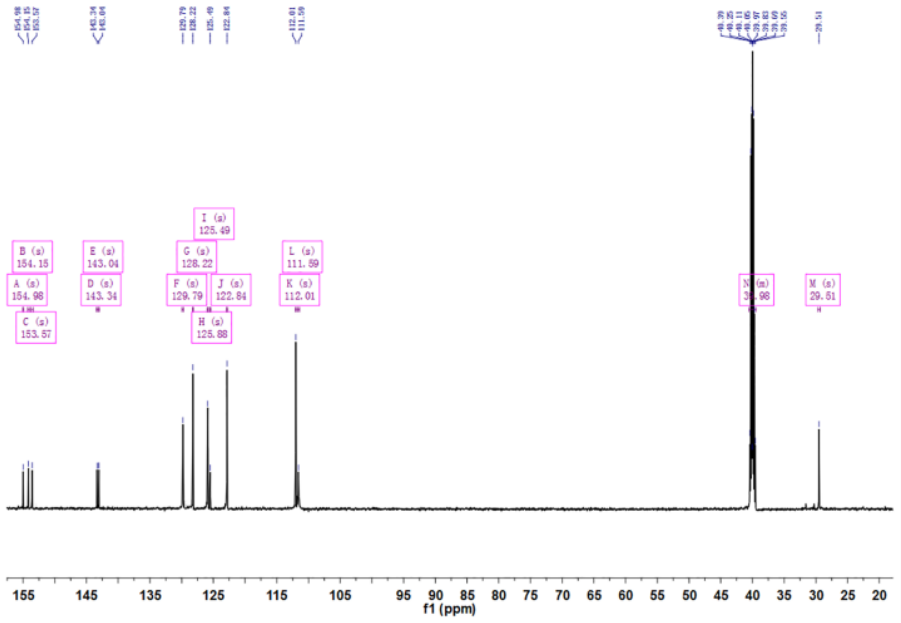


Figure S2-2. ^{13}C NMR spectra of **SPMA-AbDMA**.

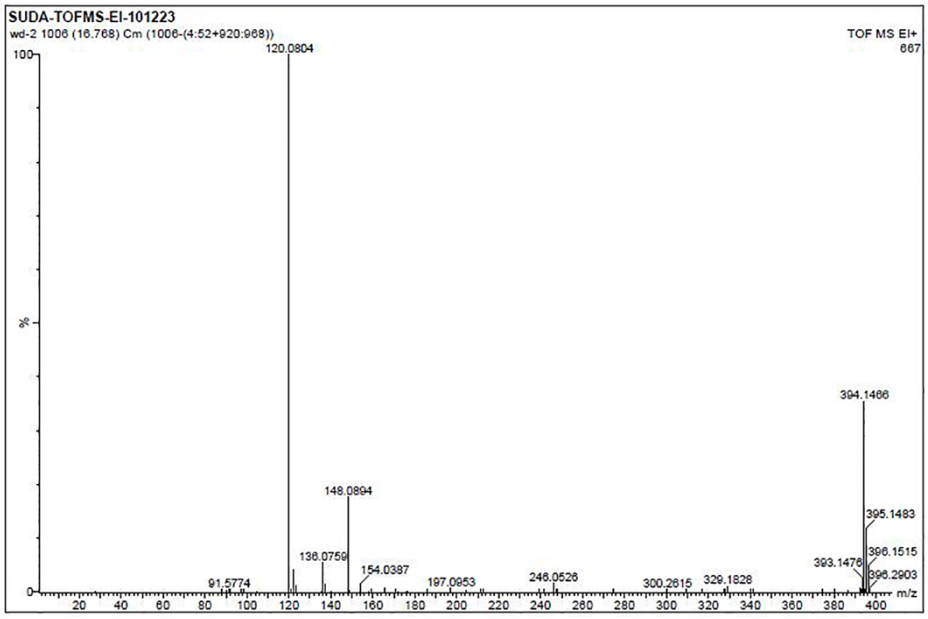


Figure S2-3. HRMS spectra of **SPMA-AbDMA.**

Thermal gravimetric analysis

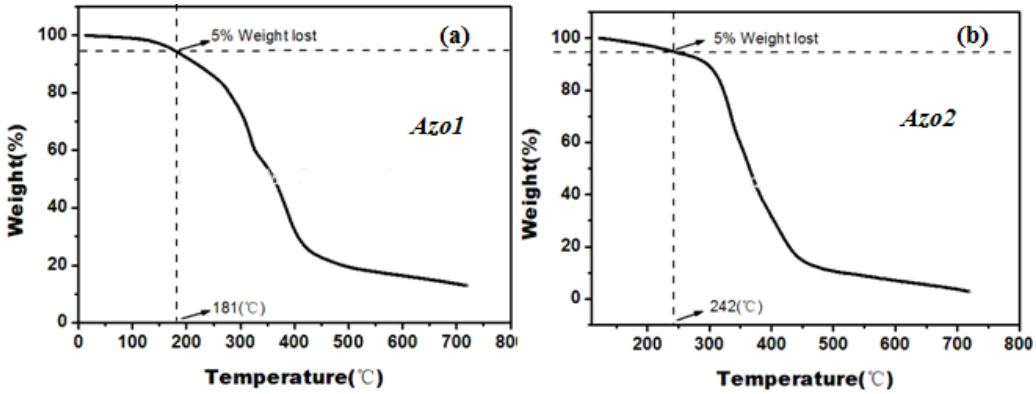


Figure S3. (a) The 5% weight-loss temperatures (T_d) of SPA-AbDMA; and (b) The 5% weight-loss temperatures (T_d) of SPMA-AbDMA.

Intermolecular interaction potential energy

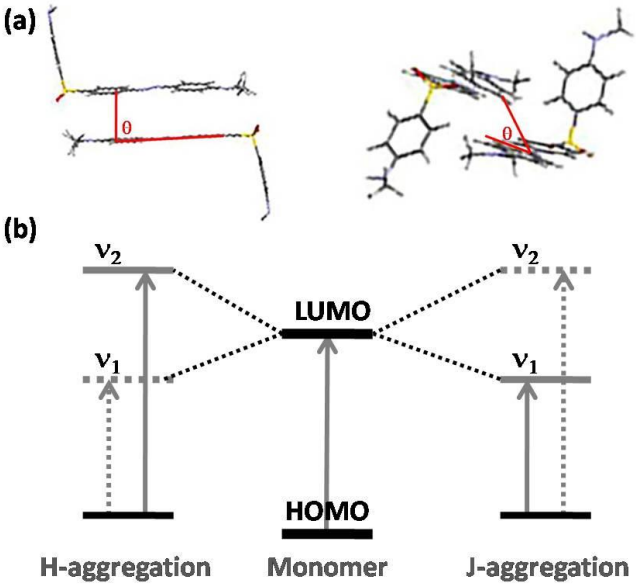


Figure S4. Scheme describing the excitonic energy state splitting, into two levels, in H-aggregated and J-aggregated materials.

Kwon and coworkers once reported that the interaction potential energy between two adjacent molecules could be approximately calculated as the equation: $V = \mu_1\mu_2(1-\cos^2\theta)/4\pi\varepsilon_0\gamma^3$, where μ_1 and μ_2 were the point dipole moment of the adjacent molecules, γ and θ were the distance vector and angle between the point dipoles.[1] Thus, the coupling interaction energy of SPA-AbDMA aggregation was larger than that of SPMA-AbDMA aggregated films, since the value of θ between SPA-AbDMA molecules was close to 90°due to the H-aggregation stacking style, while that between SPMA-AbDMA point dipoles was decreased a lot due to the J-aggregation stacking style. The increased energy of SPA-AbDMA aggregation interaction was consistent with the blue shift of the UV-Vis spectra indicating an increased energy of the excitonic states.

Optimized molecular packing

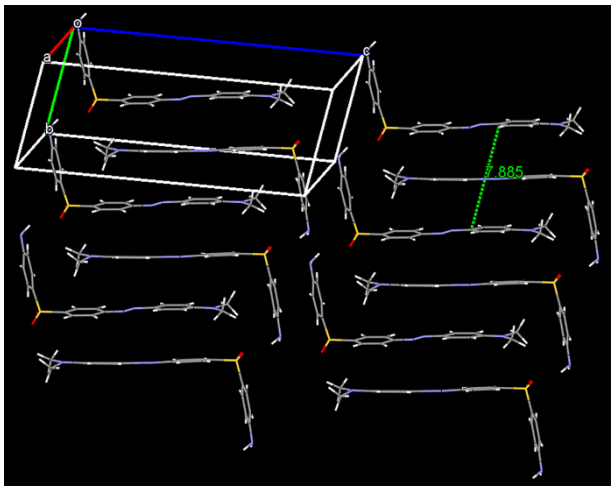


Figure S5. Optimized packed structures of SPA-AbDMA in aggregations, and the packing cell axes is 1×3×2 of a×b×c for SPA-AbDMA.

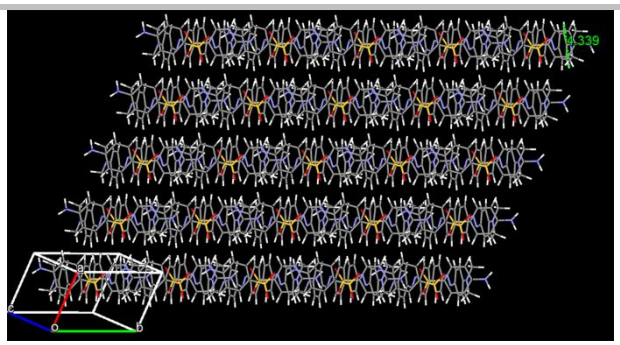


Figure S6. Optimized packed structures of SPA-AbDMA in aggregations, and the packing cell axes is 5×5×1 of a×b×c for SPA-AbDMA.

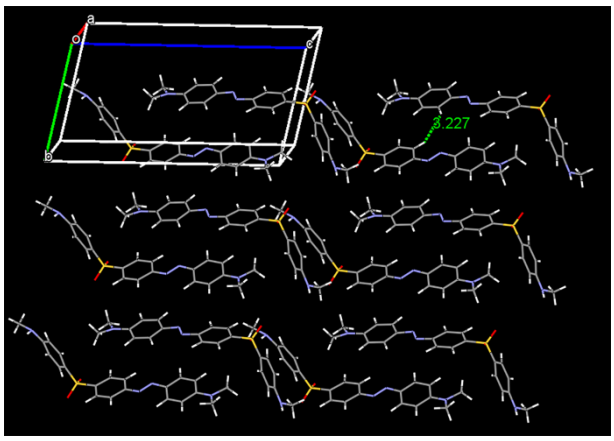


Figure S7. Optimized packed structures of SPMA-AbDMA in aggregations, and the packing cell axes is 1×3×2 of a×b×c for SPMA-AbDMA.

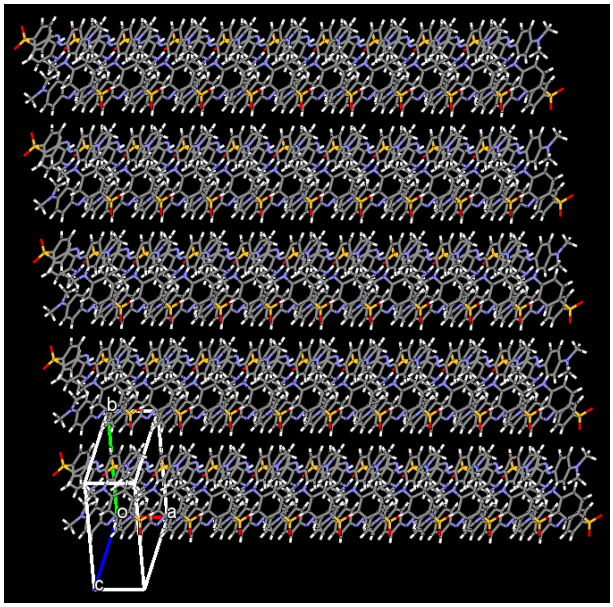


Figure S8. Optimized packed structures of SPMA-AbDMA in aggregations, and the packing cell axes is 10×5×1 of a×b×c for SPMA-AbDMA

IR absorption spectra

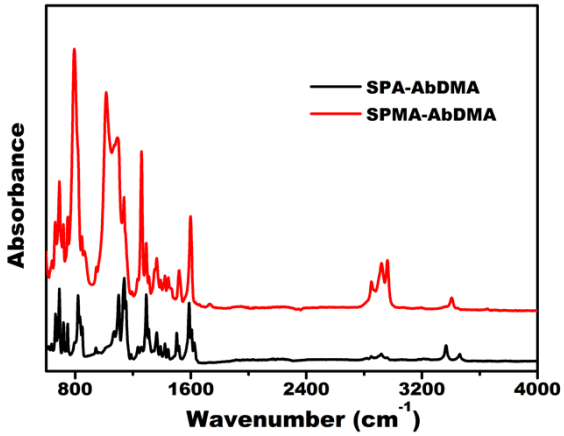


Figure S9. ATR-FTIR absorption spectra of C–H vibration modes for SPA-AbDMA and SPMA-AbDMA as a thin solid film.

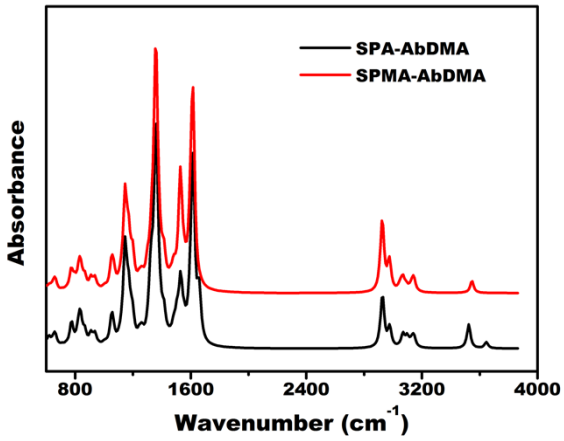


Figure S10. The simulated FTIR absorption spectra of SPA-AbDMA and SPMA-AbDMA single molecule.

Cyclic voltammogram

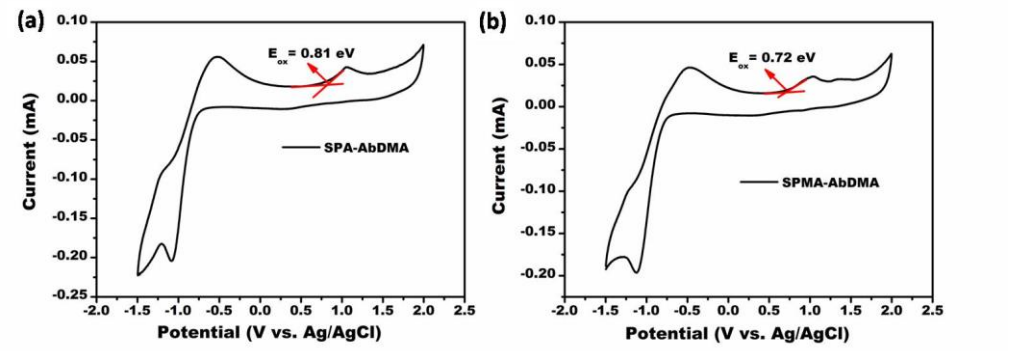


Figure S11. CV measurements of (a) SPA-AbDMA and (b) SPMA-AbDMA film in acetonitrile with 0.1M of n-Bu4NPF6 as supporting electrolyte. The scan speed is 100 mV/s.

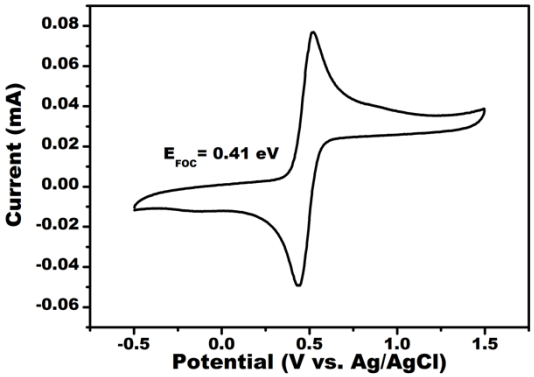


Figure S12. CV measurements of the redox standard potential of the F_c/F_c^+.

RMS of AFM

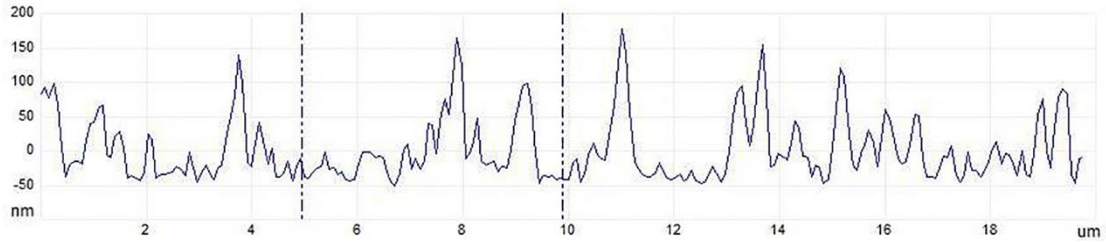


Figure S13. The room-meat-square (RMS) obtained from the surface morphology of the AFM of SPA-AbDMA.

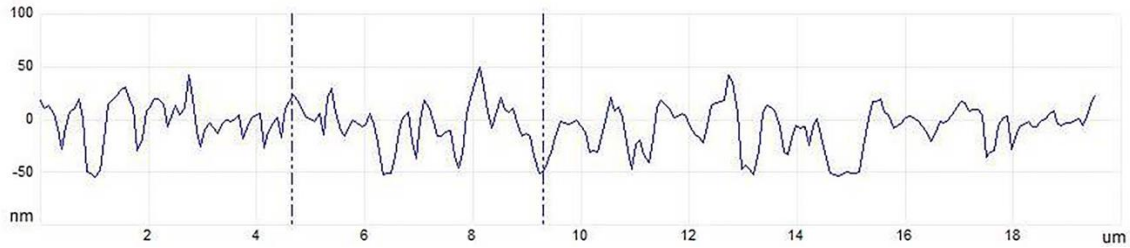


Figure S14. The room-meat-square (RMS) obtained from the surface morphology of the AFM of SPMA-AbDMA.

References

[1] S. O. Kim, T. K. An, J. Chen, I. Kang, S. H. Kang, D. S. Chung, C. E. Park, Y. H. Kim and S. K. Kwon, *Adv. Funct. Mater.*, 2011, **21**, 1616-1623.