Poly(2,6-aminoazulene): Synthesis, Photophysical Properties, and Proton Conductivity

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Table S1. Oxidation potential, HOMO and LUMO energies of pristine and protonated aminoazulene monomer, dimer and polymers **3**, **5**, **6**, and **16-18**.

compound	$\mathrm{E}_{\mathrm{ox}}\left(\mathrm{V}\right)^{a}$	$\mathrm{E}_{\mathrm{red}}\left(\mathrm{V}\right)^{a}$	HOMO $(eV)^b$	LUMO $(eV)^c$	Band gap (eV) ^d
3	0.17 ^e	-2.37 ^e	-4.98	-2.44	2.54 (3.05)
5	-0.15 ^f	-2.00 ^f	-4.66	-2.81	2.15 (2.51)
6	-0.23 ^f	-1.91 ^{<i>f</i>}	-4.58	-2.90	1.48 (1.65)
16	1.02 ^g	-	-5.83	-3.00	(2.83)
17	0.85 ^g	-	-5.66	-3.54	(2.12)
18	0.70 ^g	-	-5.51	-3.85	(1.66)

^{*a b*}Estimated by DPV relative to ferrocene/ferrocenium ion couple. ^{*b*}Estimated from the oxidation potential E_{ox}. ^{*c*}Estimated from HOMO energy and energy gap derived from UV-Vis spectra. ^{*d*}E_{LUMO}-E_{HOMO}, values in parentheses were derived from the edge of UV-Vis spectra. ^{*e*}Measured in DCM. ^{*f*}Measured in DMF. ^{*g*}Measured in TFA. **Experimental Section**

General: Gel-permeation chromatography (GPC) was performed on a Waters GPC machine with an isocratic HPLC pump (1515) and a UV detector (2487). THF or NMP was used as the eluent (flow rate = 1.0 mLmin⁻¹ for THF; 0.2 mLmin⁻¹ for NMP). Waters Styragel HR2, HR3, and HR4 columns (7.8 x 300 mm) for THF or phenogel 5 μ 500A and 5 μ 10E4A for NMP were employed for determination of the relative molecular weight with polystyrene as a standard (M_n values ranged from 966 to 1.84x10⁵). Absorption spectra were measured on a Hitachi U-3310 spectrophotometer. An ECO Chemie μ Autolab III potentiostat/galvanostat was used for the electrochemical experiments in which a Pt electrode or the polymer film was directly used as the working electrodes, a Pt electrode was used as counter electrodes and an Ag/AgCl electrode was used as the reference electrode.

2-aminoazulene (3) ^{S1}



mp 89-90 °C (Lit.^{S1} 93-94 oC); 1H NMR (400MHz, DMF-d₇) δ 6.6-6.7 (m, embodied a s at 6.63 (2 H) and a broad peak at 6.64 (2 H)), 6.9-7.1 (m, embodied a t at 7.01 (2 H) and a t at 7.06 (1 H)), 7.72 (d, *J* = 10.8 Hz, 2 H); ¹³C NMR (100 MHz, DMF-d₇) δ 103.0, 123.9, 125.8, 127.2, 142.5, 160.0; ¹H NMR (400MHz, CD₂Cl₂/ 3 eq. TFA) δ 3.82 (s, 2 H), 6.30 (s, 1 H), 7.05-7.25 (m, 3 H), 7.25-7.45 (m, 2 H), 8.3-8.6 (br, 1 H), 8.6-8.9 (br, 1 H); ¹³C NMR (100 MHz, CD₂Cl₂/TFA = 2/1) δ 42.9, 115.4, 135.8, 136.9, 139.6, 140.8, 145.9, 155.8, 175.9, 180.8.

[6-(Azulen-2-yl)amino]-2-aminoazulene (5)



Under N₂, to a solution of **10** (50 mg, 0.13 mmol) in DCM (5 mL) was added TFA (10 mL). The solution turned to pinky red immediately. After staying at rt for 1 h, solvent was removed in vacuo to afford the residue, which was taken up in DMF (5 mL), to which was added Cs_2CO_3 (50 mg). The mixture was poured into water and the precipitant was collected by filtration and washed with water, EtOH and ether to afford **5** as dark red solid (35 mg, 95%): 350 °C (dec.), ¹H NMR (DMF-d₇, 400 MHz): δ 6.22 (br, 2 H), 6.57 (s, 2 H), 7.13 (t, J = 10.8 Hz, 2 H), 7.15 (s, 2 H), 7.34 (t, J = 10.8 Hz, 1 H), 7.31 (d, J = 10.8 Hz, 2 H), 7.71 (d, J = 10.8 Hz, 2 H), 7.95 (d, J = 10.8 Hz), 9.71 (br, 1 H); ¹³C NMR (DMF-d₇, 100 MHz): δ 105.2, 116.1, 125.6, 127.2, 129.8, 130.5, 130.9, 139.9, 142.6, 143.9, 154.3, 158.2; ¹H NMR (CD₂Cl₂/TFA (2/1), 400 MHz) & 3.94 (s, 2 H), 4.22 (s, 2 H), 6.43 (s, 1 H), 6.72 (s, 1 H), 7.31 (d, *J* = 7.6 Hz, 1 H), 7.35 (d, *J* = 7.6 Hz, 1 H), 7.41 (d, J = 9.5 Hz, 1 H), 7.60 (d, J = 9.5 Hz), 7.7-8.1 (m, 5 H), 9.45 (br, 1 H); ¹³C NMR (CD₂Cl₂/TFA (2/1), 100 MHz) & 41.6, 43.6, 113.7, 129.4, 133.1, 134.6, 137.6, 139.3, 139.5, 142.0, 143.0, 145.6, 147.6, 152.3, 157.2, 170.6, 172.0, 174.7, 181.0; IR (KBr) v 3014, 2958, 2925, 2851, 1700, 1577, 1491, 1399, 1217, 1084, 892, 789, 669 cm⁻¹; HRMS (ESI) (M + H): calcd for $C_{20}H_{17}N_2$: 285.1392; found: 285.1390. **Polyaminoazulene (6):**



Under N₂, polymer **13** (20 mg) was dissolved in TFA (10 mL). The solution turned to dark red, pink and finally blue. After staying at rt for 2 h, solvent was removed in vacuo to afford the salt of **6** (21 mg, 99%): ¹H NMR (DMF-d₇, 400 MHz) δ 7.0-7.2 (br, 2 H), 7.3-7.5 (br, 2 H), 7.8-8.0 (br, 2 H), 9.7-10.0 (br, 1 H); ¹³C NMR (DMF-d₇, 125 MHz) δ 107.0, 113.1, 132.1, 135.4, 145.2, 149.5; ¹H NMR (CD₂Cl₂/TFA = 2/1, 400 MHz) δ 4.3-4.6 (br, 2 H), 7.0-7.3 (br, 1 H), 7.8-8.5 (br, 4 H); IR (KBr) v 3123, 2994, 1698, 1534, 1397, 1200, 1126, 835, 726 cm⁻¹; GPC (NMP): $M_n = 2100$, PDI = 1.31.

tert-Butyl N-(azulen-2-yl)carbamate (7).



A mixture of **3** (0.3 g, 2.1 mmol) and di-tert-butyl dicarbonate (1.37 g, 6.29 mmol) was heated at 65 °C overnight under N₂. Excess di-tert-butyl dicarbonate was then removed in vacuo, and the residue was chromatographed on silica gel (toluene) to give **7** as a purple solid (0.23 g, 45 %): mp 104-105 °C; ¹H NMR (CDCl₃, 400 MHz): δ 1.57 (s, 9 H), 7.12-7.19 (m, embodied a t at 7.16 (*J* = 9.8 Hz) and a broad peak at 7.18, 3 H), 7.24 (br, 2 H), 7.41 (t, *J* = 9.8 Hz, 1 H), 8.09 (d, *J* = 9.8 Hz, 2 H); ¹³C NMR (CDCl₃, 100 MHz): δ 28.4, 81.1, 105.4, 124.1, 132.7, 133.2, 140.0, 146.4, 152.1; IR (KBr) v 3400, 3044, 3013, 2976, 2933, 1714, 1576, 1539, 1462, 1442, 1369, 1277, 1231, 1155, 1054, 797, 724, 586 cm⁻¹; HRMS (FAB) (M): calcd for C₁₅H₁₇NO₂: 243.1259; found: 243.1255.

tert-Butyl N-(6-bromoazulen-2-yl)carbamate (8).



In a manner similar to that described above, a mixture of $4^{S1,2}$ (1.0 g, 4.5 mmol) and ditert-butyl dicarbonate (2.0 g, 9.2 mmol) was transformed to **8** as a dark purple crystal (1.2 g, 83%): mp 153-154 °C; ¹H NMR (CDCl₃, 400 MHz): δ 1.57 (s, 9 H), 7.19 (br, 1 H), 7.25 (s, 2 H), 7.49 (d, *J* = 10.8 Hz, 2 H), 7.79 (d, *J* = 10.8 Hz, 2 H); ¹³C NMR (CDCl₃, 100 MHz): δ 28.2, 81.3, 107.0, 127.2, 129.4, 130.5, 138.5, 146.8, 151.8; IR (KBr) v 3371, 3097, 3041, 3008, 2968, 2967, 2931, 1711, 1572, 1536, 1449, 1366, 1243, 1156, 1055, 1027, 982, 874, 823, 788, 635, 600, 512 cm⁻¹; HRMS (FAB) (M): calcd for C₁₅H₁₆NO₂: 321.0364; found: 321.0360.

tert-Butyl N-(6-bromoazulen-2-yl)-N-methylcarbamate (9).



Under N2, NaH (34 mg, 60 wt%, 0.84 mmol) was added to a vigorously stirred solution

of **8** (0.18 g, 0.56 mmol) in anhydrous DMF (6 mL) at 0 °C, the color of the solution became darker immediately. After 15 min, methyl iodide (0.17 mL, 2.8 mmol) was syringed, and the mixture was further stirred for 1 h at rt then quenched with water (0.1 mL, 6 mmol). Diethyl ether (15 mL) was added, and the organic layer was washed sequentially with water (3x10 mL), brine (1x10 mL), water (1x10 mL) and dried (Na₂SO₄). Part of the solvent was removed in vacuo. Pentane was then added and **9** was precipitated as a dark purple solid (0.27 g, 91%): mp 153-154 °C; ¹H NMR (CDCl₃, 400 MHz): δ 1.61 (s, 9 H), 3.49 (s, 3 H), 7.37 (s, 2 H), 7.49 (d, *J* = 10.8 Hz, 2 H), 7.82 (d, *J* = 10.8 Hz, 2 H); ¹³C NMR (CDCl₃, 100 MHz): δ 28.4, 35.7, 82.0, 110.0, 127.2, 129.7, 130.9, 138.0, 151.4, 153.2; IR (KBr) v 3017, 2978, 2931, 1710, 1567, 1529, 1501, 1429, 1367, 1307, 1160, 1134, 1097, 820 cm⁻¹; HRMS (ESI) (M+H): calcd for C₁₆H₁₉NO₂Br: 336.0599; found: 336.0596.

tert-Butyl (N-{6-[(azulen-2-yl)amino]})azulen-2-ylcarbamate (10).



A mixture of $\mathbf{3}^{S1}$ (68.5 mg, 0.478 mmol), $\mathbf{8}$ (140 mg, 0.435 mmol), Cs_2CO_3 (290 mg, 0.90 mmol), Pd(dba)₂ (9.9 mg, 0.017 mmol), dippf (16.4 mg, 0.0392 mmol) in anhydrous THF (2 mL) was degassed by freeze-pump-thaw (3 cycles) and then refluxed for 2 h. After cooling to rt, the solution was passed through a celite bed (2 cm) and washed with THF. The filtrate was chromatographed on silica gel (CHCl₃/toluene=1/3) to afford **10** as an dark red solid (121 mg, 72%): 156 °C (dec.); ¹H NMR (CD₂Cl₂, 400 MHz): δ 1.55 (s, 9 H), 7.15-7.20 (m, embodied a singlet at 7.13, a broad peak at 7.14, and a triplet centered at 7.16 (J = 10.0 Hz), 7 H), 7.22-7.27 (m, embodied a dd at 7.25 ($J_1 = 1.2$ Hz, $J_2 = 9.6$ Hz) and a broad peak at 7.25, 3 H), 7.34 (tt, $J_1 = 1.2$ Hz, $J_2 = 10.0$ Hz, 1 H), 7.99 (dd, $J_1 = 1.2$ Hz, $J_2 = 10.0$ Hz, 2 H), 8.01 (dd, $J_1 = 1.2$ Hz, $J_2 = 9.6$ Hz, 2 H); ¹³C NMR ((CD₃)₂CO, 100 MHz): δ 28.6, 80.1, 105.7, 107.8, 114.3, 125.2, 131.0, 131.9, 133.0, 136.5, 141.7, 144.9, 148.3, 151.7, 153.2; IR (KBr) v 3325, 3007, 2973,

2927, 1706, 1580, 1531, 1499, 1406, 1239, 1223, 1153, 1050, 792 cm⁻¹; HRMS (FAB) (M+H): calcd for C₂₅H₂₅N₂O₂: 385.1916; found: 385.1911.

tert-Butyl 6-[N-(azulen-2-yl)-N-(*tert*-butoxycarbonyl)amino]azulen-2-yl)carbamate (11).



Under N₂, a mixture of molecular sieve (20 mg, 4 Å) and Cs₂CO₃ (39.12 mg, 0.12 mmol), formerly heated under vacuum at 190 °C for 10 h, was added a solution of 7 (14.8 mg, 0.061 mmol), **9** (20.0 mg, 0.059 mmol), (Pd(ally)₂Cl)₂ (0.44 mg, 0.0012 mmol) and JackiePhos (2.39 mg, 0.003 mmol) in anhydrous toluene (0.7 mL) and the mixture was heated at 75 °C overnight. After cooling, the mixture was passed through a celite bed (3 cm) and the solvent was removed in vacuo. The residue was chromatographed on silica gel (DCM/hexane = 1/3). The first band was recovered **7** (3.3 mg, 22%), the second band was **11** (18 mg, 63%) as a purple red solid: mp 145-146 °C; ¹H NMR (CDCl₃, 400 MHz): δ 1.47 (s, 9 H), 1.63 (s, 9 H), 3.55 (s, 3 H), 7.10 (s, 2 H), 7.13 (t, *J* = 9.8 Hz, 2 H), 7.19 (d, *J* = 10.8 Hz, 2 H), 7.41 (t, *J* = 9.8 Hz, 1 H), 7.45 (s, 2 H), 8.04 (d, *J* = 9.8 Hz, 2 H), 8.17 (d, *J* = 10.8 Hz, 2 H); ¹³C NMR (CDCl₃, 100 MHz): δ 28.3, 28.5, 35.8, 82.0, 82.1, 108.5, 108.7, 124.0, 125.4, 131.7, 133.5, 133.7, 138.8, 139.2, 145.2, 150.8, 151.5, 152.6, 153.3; IR (KBr) v 3013, 2970, 2928, 1714, 1488, 1403, 1366, 1291, 1274, 1254, 1152, 849, 800 cm⁻¹; HRMS (ESI) (M+H): calcd for C₃₁H₃₅N₂O₄: 499.2597; found: 499.2598.

Poly[2-(tert-butoxylcarbonyl)aminoazulene] (13):



A mixture of molecular sieve (80 mg, 4 Å) and Cs₂CO₃ (280 mg, 0.86 mmol) was heated under vacuum at 190 °C for 10 h. Under N₂, a solution of **8** (146 mg, 0.45 mmol), (Pd(ally)₂Cl)₂ (3.21 mg, 0.0088 mmol) and Jackie Phos (13.5 mg, 0.017 mmol) in anhydrous toluene (3 mL) was then added and the mixture was heated at 75 °C for 8 h. After cooling, the mixture was passed through a celite bed (3 cm) and washed with DCM. Part of the solvent was removed in vacuo, then diethyl ether was added and the precipitant was collected by centrifuge, and the solid was redissolved in DCM. This process was repeated several times using different combinations of mixed solvents (DCM with diethyl ether, CH₃OH, and pentane), and the residue was dried at 60 °C under vacuum overnight to yield **13** as an orange red solid (58 mg, 52%): ¹H NMR (CDCl₃, 400 MHz): δ 1.3-1.7 (br, 9 H), 7.0-7.3 (br, 4 H), 8.0-8.1 (br, 2 H); ¹³C NMR (CDCl₃, 100 MHz): δ 28.2, 82.5, 109.7, 125.6, 132.2, 138.8, 145.4, 152.0, 152.5; IR (KBr) v 3002, 2976, 2930, 1718, 1572, 1541, 1488, 1405, 1368, 1286, 1252, 1153, 1053, 847, 643 cm⁻¹;GPC (NMP): M_n = 2900, PDI = 1.22.

Time of flight experiments.^{S2} The device for TOF measurements was prepared using the following configuration: glass/ITO (130nm)/PAAz-H⁺(2.2 μ m) or PAAz(1.5 μ m) /Ag (200nm) with an active area of 2x2 mm². Patterned indium-tin-oxide (ITO) glass substrates were cleaned in an ultrasonic bath using deionized water and 2-propanone in succession for 20 min each. A solution of **18** in TFA was drop-casted onto the substrates and then dried in air at room temperature for 15 min followed by baking at 90°C for 2 min to remove residual TFA. A film of **6** was obtained by immersing the above-mentioned film prepared from **18** in TEA for 12 h. Silver was then thermally evaporated on the organic solid film as the counter electrode, and it was acted as a blocking contact

to ensure that no charge could be injected from the contact interface under bias. The sample was encapsulated under dry nitrogen to avoid degradation due to ambient oxygen and water. In the TOF mobility measurement (Figure S1), frequency-doubled (532nm) and frequency-tripled (355nm) Nd:YAG laser were used for pulsed illumination (~6.5ns) through the transparent ITO electrode for **18** and **6**, respectively. Under an applied electric field, a transient current contributed by the photo-generated charges was recorded by oscilloscope.



Figure S1. The schematic illustration of TOF measurement.

The carrier mobility μ is then given by

$$\mu = \frac{D}{t_{\tau}E} = \frac{D^2}{Vt_{\tau}}$$

where *D* is the sample thickness, *E* is the applied electric field, and *V* is the applied bias. Depending on the polarity of the continuous bias voltage on the sample, the carrier we interest (holes or electrons) is selected to sweep across the organic layer with a transit time of t_{τ} .

Charge mobilities for 18. Representative TOF transient currents for the electrons and holes of **18** are shown in Fig. S2(a) and (b), respectively. Here, a bias voltage of 65 V was applied to a 2.2µm-thick film of **18**. Analysis indicates the dispersive electron and hole transport characteristics of **18**. In the double-logarithmic representation (insets of Fig. 2), the carrier transit time, t_{τ} , was discerned from the intersection point of two asymptotes. Electron and hole mobilities of **18** are shown as a function of $E^{1/2}$ in Fig. S3. It shows weak electric field dependence of both hole and electron mobilities. The hole mobilities were about 3 x 10⁻⁶ cm²V⁻¹s⁻¹ and the electron mobilities were ranged from 2.8 x 10⁻⁶ cm²V⁻¹s⁻¹ to 4.8 x 10⁻⁶ cm²V⁻¹s⁻¹ under the applied field from 2.3 x 10⁵





Figure S2. TOF transients for **18** (2.2 μ m) at E = 2.9 x 10⁵ V/cm: (a) electron and (b) hole. Inset: double logarithmic plot.



Figure S3. Hole and electron mobilities vs. $E^{1/2}$ for **18**.

Charge mobilities for 6. Representative TOF transient currents for the electrons and holes of **6** are shown in Figure S4a and b, respectively. Here, a bias voltage of 70 V was applied to a 1.5 μ m-thick film of **6**. Analysis reveals the dispersive electron and hole transport features of **6**. Electron and hole mobilities of **6** are shown as a function of $E^{1/2}$ in Fig. S5. It shows negative electric field dependence of both hole and electron mobilities. The hole mobilities were ranged from 7.4 x 10⁻⁶ to 3.1 x 10⁻⁶ cm²V⁻¹s⁻¹ and the electron mobilities were about 3 x 10⁻⁶ cm²V⁻¹s⁻¹ under the applied

filed from 3.6×10^5 to 4.6×10^5 V/cm.



Figure S4. TOF transients for 6 (1.5 μ m) at E = 4.7 x 10⁵ V/cm: (a) electron and (b) hole. Inset double logarithmic plot.



Figure S5. Hole and electron mobilities vs. $E^{1/2}$ for **6**.

Preparation and Characterization of Nafion/18 composite membrane. Compound **13** (3 mg) was dissolved in TFA (0.3 mL) and stayed at room temperature for 4 h for *in situ* deprotection. The solvent was then removed under vacuum to afford **18** which was homogeneously dispersed in a solution of Nafion 115 (60 mg) in DMF (0.3 mL). The resulting mixture was then poured into a circular Teflon dish with an area of 6 cm². The mixture was stay at 60 °C for 72 h to allow slow evaporation of DMF, and the residual solvent was then removed under vacuum at 60°C for one day to afford a dry, black film (Figure S6). The film was then pealed off from the dish and immersed in 1 M sulfuric acid at 50°C for 4 h. The acid-treated film was then washed with copious water to remove excess acid to generate a fully hydrated Nafion/**18** composite membrane. Similar procedure was adopted on pristine Nafion 115 solution to afford the reference Nafion membrane.



(a)

(b)

Figure S6. Pictures of (a) prestine Nafion and (b) Nafion/18 membranes.

Water uptake. The surface water of a hydrated membrane was wiped off using a tissue paper before measuring the weight of a hydrated membrane, denoted as W_{wet} . The weight of a dried membrane, W_{dry} , was measured after drying the membrane overnight under vacuum at 60 °C. The water uptake (WU in wt %) was calculated as

WU (wt%) =
$$(W_{wet} - W_{dry})/W_{dry} \times 100$$
 (1)

Proton Conductivity. The proton conductivity of the fully hydrated membrane was measured at room temperature using alternating-current (AC) impedance analyzer Biologic SP-200 with a through-plane setup using platinum electrodes with 1 mm diameter. The impedance measurement was carried out from 7 MHz to 1 Hz at a voltage amplitude of 10 mV (Figure S7). The conductivity was calculated from the following equation

$$\sigma = \ell / R x A \qquad (2)$$

where σ is the proton conductivity (S cm⁻¹), ℓ is the thickness of membranes (cm), R is the ohmic resistance of the membrane reading from the Nyquist diagram, and A is the area of the electrode (cm²).



Figure S7. The through-plane cell of AC impedence measurement and the Nyquist diagram of the fully hydrated Nafion/**18**.

Methanol and water permeability. Methanol permeability was measured at room temperature by a side-by-side glass diffusion cell. Forty milliliter of 6M methanol solution and 40 mL deionized water were placed at the two opposite sides of the membrane. Methanol flux and water flux were established across the membrane due to the concentration difference between the two compartments. The methanol flux and the methanol permeability could be retrieved using eq (3) and eq (4), respectively .

$$Flux = [W_{MeOH}/M_{MeOH}]/A \times t$$
(3)
$$P_{MeOH} = [Flux_{MeOH} \times \ell]/\Delta C_{MeOH}$$
(4)
$$P_{water} = [Flux_{water} \times \ell]/DC_{water}$$
(5)

where W_{MeOH} is the total weight of methanol diffused, M is the molecular weight of methanol, t (sec) is the time allowed for the permeation experiment, A (cm²) and ℓ (cm) are the effective area for diffusion and the thickness of the membrane, ΔC_{MeOH} is the average difference in the molar concentration of methanol between the two sides of the membrane throughout the experimental period. Similar equation of water permeability can be deduced from eq 5.

DFT calculations

The bond lengths of each C-N bonds in aminoazulene monomer, dimer and trimer (as model structures, **Ma-c**) were estimated by density functional theory $(DFT)^{S3}$ calculations at GGA/BLYP/DNP level, implemented with the DMol³ program package.^{S4} Convergence thresholds of energy, force, displacement and self-consistent field (SCF) density for geometry optimizations were 2×10^{-5} Hartree, 0.004 Hartree/Å, 0.005 Å and 1×10^{-5} Hartree, respectively. Neither Direct Inversion of Iterative Subspace (DIIS) nor smearing techniques were used, as to obtain precise results. The results are shown below. The bond lengths of each C-N bonds are labeled on the structures.





Figure S8. Model structures Ma-c

	АТОМ	Х	Y	Z
1	С	0.000000	0.000000	-2.294483
2	С	-1.156477	0.000000	-1.472972
3	С	-0.747336	0.000000	-0.133230
4	С	0.747336	0.000000	-0.133230
5	С	1.156477	0.000000	-1.472972
6	С	1.590932	0.000000	0.981555
7	С	1.263221	0.000000	2.340706
8	С	0.000000	0.000000	2.942478
9	С	-1.263221	0.000000	2.340706
10	С	-1.590932	0.000000	0.981555
11	Ν	0.000000	0.000000	-3.662237
12	н	-0.867562	0.000000	-4.186397
13	н	0.867562	0.000000	-4.186397
14	н	-2.187926	0.000000	-1.823006
15	н	2.187926	0.000000	-1.823006
16	н	2.662293	0.000000	0.752732
17	н	2.113397	0.000000	3.029341
18	н	0.000000	0.000000	4.036783
19	н	-2.113397	0.000000	3.029341
20	н	-2.662293	0.000000	0.752732

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Energy: -441.2683279 Hatree

	АТОМ	х	Y	Z
1	с	-6.059780	2.233031	0.441098
2	С	-5.584735	0.931217	0.632538
3	С	-4.284437	0.438503	0.490668
4	С	-3.122141	1.113839	0.107818
5	С	-2.994903	2.552150	-0.266918
6	С	-4.007136	3.517018	-0.274382
7	С	-5.359476	3.379598	0.044586
8	С	-1.652518	2.766578	-0.599500
9	С	-0.954634	1.536393	-0.479186
10	С	-1.852913	0.533456	-0.033287
11	Ν	0.379975	1.401814	-0.808799
12	С	2.342246	0.229256	-1.446120
13	С	1.286673	0.366118	-0.519674
14	С	1.093496	-0.378776	0.661830
15	С	1.835799	-1.445721	1.158696
16	С	2.974273	-2.076706	0.646571
17	С	3.716592	-1.708691	-0.582579
18	С	3.404201	-0.670156	-1.463625
19	С	4.800475	-2.594688	-0.690386
20	С	4.768499	-3.475690	0.417655
21	С	3.648314	-3.160958	1.227546
22	Н	0.750715	2.143515	-1.399480
23	Н	-7.129213	2.375365	0.622755
24	н	-6.333389	0.196734	0.941628
25	н	-4.153634	-0.628026	0.702232
26	н	-3.690056	4.520985	-0.573969
27	н	-5.956472	4.292643	-0.036531
28	н	-1.214415	3.718307	-0.899740
29	Н	-1.624610	-0.519589	0.106596
30	Н	2.304682	0.922428	-2.293307
31	Н	0.267302	-0.044754	1.291056
32	н	1.477428	-1.848977	2.111696

33	н	4.084863	-0.559841	-2.314401
34	н	5.542206	-2.599839	-1.488680
35	Ν	5.645437	-4.528710	0.635083
36	н	3.360295	-3.674440	2.144828
37	н	6.552629	-4.430523	0.178302
38	н	5.738362	-4.822859	1.607381

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Energy: -881.3484093 Hatree

	АТОМ	х	Y	Z
1	С	5.159613	-1.076354	3.124030
2	С	4.271924	-0.926266	2.036418
3	С	4.617140	-0.732666	0.683849
4	С	5.876206	-0.570938	0.109000
5	С	7.146708	-0.572368	0.691544
6	С	7.465155	-0.800234	2.121435
7	С	6.549372	-1.033146	3.152879
8	С	8.861437	-0.748267	2.247546
9	С	9.415611	-0.501614	0.966766
10	С	8.367027	-0.395618	0.021177
11	н	4.676669	-1.233027	4.094444
12	н	3.778481	-0.737942	-0.013611
13	н	5.866566	-0.435084	-0.977847
14	н	6.993841	-1.181385	4.142887
15	н	9.423526	-0.877587	3.171796
16	Ν	10.764937	-0.321364	0.694640
17	н	8.487044	-0.206722	-1.045525
18	С	-9.637829	-0.577068	-2.825462
19	С	-8.702056	-1.535386	-2.420650
20	С	-7.386331	-1.352735	-1.985090
21	С	-6.659269	-0.167084	-1.848298
22	С	-7.129911	1.217452	-2.140341
23	С	-8.393570	1.606855	-2.595688
24	С	-9.503180	0.815273	-2.898496
25	С	-6.055613	2.074008	-1.879351

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26	С	-4.950095	1.294751	-1.447993
27	С	-5.324641	-0.073692	-1.424669
28	Ν	-3.719603	1.860258	-1.174076
29	С	-1.368255	1.947395	-0.908572
30	С	-2.584642	1.333276	-0.537686
31	С	-2.762620	0.315469	0.422794
32	С	-1.806403	-0.360833	1.174804
33	С	-0.412398	-0.230731	1.199718
34	С	0.401447	0.731066	0.424717
35	С	-0.072334	1.688425	-0.479665
36	С	1.743823	0.526061	0.772065
37	С	1.796335	-0.525382	1.723523
38	С	0.476835	-0.980086	1.983105
39	н	-3.594556	2.796247	-1.555505
40	н	-10.613679	-0.970239	-3.125636
41	н	-9.048424	-2.572563	-2.446118
42	н	-6.843519	-2.265091	-1.716154
43	н	-8.521881	2.683646	-2.747433
44	н	-10.386317	1.357325	-3.248882
45	н	-6.065158	3.158677	-1.982154
46	н	-4.680693	-0.915927	-1.187935
47	н	-1.459373	2.728806	-1.670166
48	н	-3.800217	0.052221	0.632414
49	н	-2.212751	-1.102800	1.869949
50	н	0.700027	2.312792	-0.941106
51	н	2.585569	1.112124	0.412147
52	Ν	2.909691	-1.035959	2.366701
53	н	0.204685	-1.786995	2.663416
54	н	2.715423	-1.538738	3.230155
55	н	11.401583	-0.759832	1.359215
56	н	11.038643	-0.510400	-0.269023

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Energy: -1321.4281174 Hatree

References

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Figure S10. GPC result of polymer 13.



Figure S11. GPC result of polymer 6.

Photophysical results



Figure S12. Absorption spectra of (a) 13 (b) 10 and (d) 6 in different solvents.



Figure S13. Time-dependent absorption spectra of polymer **13** in TFA/DCM (1/5) cosolvent measured in every 30 min. The spectra remained unchanged after 240 min.



Figure S14. Normalized absorption spectra of polyaminoazulene **6** in NMP (solid), in TFA/NMP (1/10) (dotted) and its protonated form (**18**) in TFA/DCM (1/5) (dash). The dash- dotted line shows the absorption spectrum of protonated polyaminoazulene **6** dissolved in NMP.



Figure S15. (a) and (c) DPV of **3** (solid), **5** (n = 1) (dash), and **6** (dotted) in DMF, using TBAP as electrolytes. (b) DPV of **16** (solid), **17** (dash) and **18** (dotted) in TFA, using triethylammonium trifluoroacetate as electrolytes.

Figure S16. ¹H NMR spectrum of 5.











Figure S19. 13C NMR spectrum of 6 in DMF-d₇.

2000 100 2001 1



Figure S20. ¹H NMR spectrum of **7**.



Figure S21. ¹³C NMR spectrum of 7.



Figure S22. ¹H NMR spectrum of 8.



udd -000.0-20 802.82 40 60 822.18-56.556 702.826 702.826 8 100 0 IZ ω 966.901-120 120.468 129.435 Б 140 274.851-852.951 £18.121-160 Pulse Sequence: s2pul 180

Figure S23. ¹³C NMR spectrum of 8.

Figure S24. ¹H NMR spectrum of 9.



Figure S25. ¹³C NMR spectrum of 9.



Figure S26. ¹H NMR spectrum of 10.





Figure S27. ¹³C NMR spectrum of 10 in acetone-d₆.

Figure S28. ¹H NMR spectrum of 11.





Figure S29. ¹³C NMR spectrum of 11.

Figure S30. ¹H NMR spectrum of 13.



Figure S31. ¹³C NMR spectrum of 13.



Figure S32. ¹H NMR spectrum of 16.



Figure S33. ¹³C NMR spectrum of 16.



Figure S34. ¹H NMR spectrum of 17 in CD₂Cl₂.





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