

Supplementary Information

Azobenzene Based Inorganic Salts for Light Modulated Ionic Conductivity in Aqueous Solution

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1. Synthesis

The synthesis and characterization of azobenzene compounds are shown in Scheme 1. 4,4'-azodibenzoic acid was synthesized as reported¹⁻². Azobenzene based inorganic compounds were prepared through neutralization reactions of 4,4'-azodibenzoic acid with lithium hydroxide, sodium hydroxide and potassium hydroxide respectively.

Synthesis of 4,4'-azodibenzoic acid (Azo-H)

Sodium hydroxide solution (5.6m, 150mL) was dropped into 4-Nitrobenzoic acid solution (10g in 50mL water) under water reflux at 50 °C. Then a hot glucose solution (61.5g in 200mL water) was slowly added and the reaction was under airflow for 24h at 50 °C to yield a noticeable precipitate. The reaction mixture was filtered and washed by concentrated hydrochloride solutions. The final product was washed by the water three times and dried under vacuum at 80 °C. ¹H NMR (δ ppm, DMSO): 8.05 (m, 2H), 8.03 (m, 2H), 7.93 (m, 2H), 7.91 (m, 2H). HRMS for C₁₄H₁₆N₂O₄ (calculated at 270.24): found m/z=269.06([M-H]⁺). Elemental analysis for C₁₄H₁₆N₂O₄, Calc.: C, 62.22; H, 3.73; N, 10.37; O, 23.68. Found: C, 62.56; H, 3.22; N, 9.95; O, 24.27.

Synthesis of lithium (E)-4,4'-(diazene-1,2-diyl)dibenzoate (Azo-Li)

4,4'-azodibenzoic acid (1.0 g, 3.7mmol) was stirred in water with dropwise of lithium hydroxide (0.09g, 3.6mmol) solution at room temperature. After 24h, the mixed solvent was filtered to remove the unreacted 4,4'-azodibenzoic acid and the product was washed by ethanol several times to obtain yellow product, Azo-Li. ¹H NMR (δ ppm, D₂O): 8.05 (m, 2H), 8.03 (m, 2H), 7.93 (m, 2H), 7.91 (m, 2H). HRMS for C₁₄H₁₆N₂O₄ (calculated at 270.24): found m/z=269.06([M-2Li+H]⁺). Elemental analysis for C₁₄H₁₄N₂O₄Li₂, Calc.: C, 59.61; H, 2.86; Li, 4.92; N, 9.93; O, 22.68. Found: C, 59.63; H, 2.80; Li, 5.01; N, 9.93; O, 22.64.

Synthesis of sodium (E)-4,4'-(diazene-1,2-diyl)dibenzoate (Azo-Na)

4,4'-azodibenzoic acid (1.0 g, 3.7mmol) was stirred in water at room temperature and sodium hydroxide (0.14g, 3.6mmol) solution was added dropwise. After 24h, the mixed solvent was filtered to remove the unreacted azobenzene and the product was washed by ethanol several times to obtain yellow product, Azo-Na. ¹H NMR (δ ppm, D₂O): 8.06 (m, 2H), 8.04 (m, 2H), 7.94 (m, 2H), 7.92 (m, 2H). HRMS for C₁₄H₁₄N₂O₄Na₂ (calculated at 270.24): found m/z=269.06([M-2Na+H]⁺). Elemental analysis for C₁₄H₁₄N₂O₄Li₂, Calc.: C, 53.52; H, 2.57; N, 8.92; Na, 14.63; O, 20.37. Found: C, 53.70; H, 2.55; Na, 14.55; N, 8.92; O, 20.28.

Synthesis of potassium (E)-4,4'-(diazene-1,2-diyl)dibenzoate (Azo-K)

4,4'-azodibenzoic acid (1.0 g, 3.7mmol) was stirred in water with dropwise of potassium hydroxide (0.2g, 3.6mmol) solution at room temperature. After 24h, the mixed solvent was filtered to remove the unreacted azobenzene and the product was washed by ethanol several times to obtain yellow product, Azo-K. ¹H NMR (δ ppm,

D₂O): 8.07(m, 2H), 8.05 (m, 2H), 7.95 (m, 2H), 7.92 (m, 2H). ESI-MS for C₁₄H₁₄N₂O₄K₂ (calculated at 270.24): found 269.06([M-2K+H]⁺). Elemental analysis for C₁₄H₁₄N₂O₄Li₂, Calc.: C, 48.54; H, 2.33; K, 22.57; N, 8.09; O, 18.47; Found: C, 48.55; H, 2.61; K, 22.80; N, 8.02; O, 18.24.

2. Sample preparation and Measurements

An appreciate amount of the azobenzene compound and water was mixed and stirring for 24 h before conducting experiments. UV-vis spectra were carried out on a UV-Vis instrument. The spectrum was recorded in a wavelength range from 200 nm to 650 nm with a step of 1nm, and deionized waster was used as the blank. Viscosity measurements were performed on Haake Mars using a 25 mm diameter cylindrical rotor. A gap spacing of approximately 0.2 mm was used for all experiments. The impedance spectra of electrochemical impedance spectroscopy (EIS) were recorded on an EG&G Princeton Applied Research P4000+ workstation (10 mHz~1 MHz, 0.01 mV). The sample temperature was controlled by a WT-3000 hot-stage. The sandwiched samples were heated to 60 °C and kept for 30 min before measuring at room temperature. Several rough scanning measurements were utilized to ensure the proper measuring frequency. Photo-irradiation with selective intensity and wavelength (UV light: 366 nm, 30 mW cm⁻²; visible light: 450 nm, 15 mW cm⁻²) was utilized for isomerization of azobenzene compounds. Transmission Electron Microscope (TEM, Hitachi) measurements was conducted by dropping sample solutions on copper grid. Raman spectroscopy was conducted on a Jasco RMP-300 and thermal gravimetric analysis (TGA) was carried out on a Hatachi STA7200 by

heating from 30 to 550 °C at a heating rate of 10 °C/min. Elemental analysis(EIS) measurements were performed in Agilent ICP-OES730 with Elementar Vario EL cube. High resolution mass spectra (HRMS) were conducted on TSQ quantum ultra in negative modes.

3. Figures

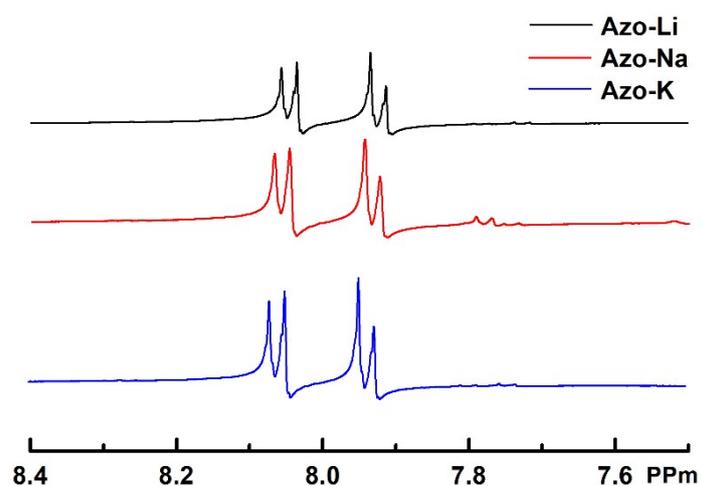


Figure S1. ¹H NMR of Azo-Li, Azo-Na and Azo-K in D₂O in the dark.

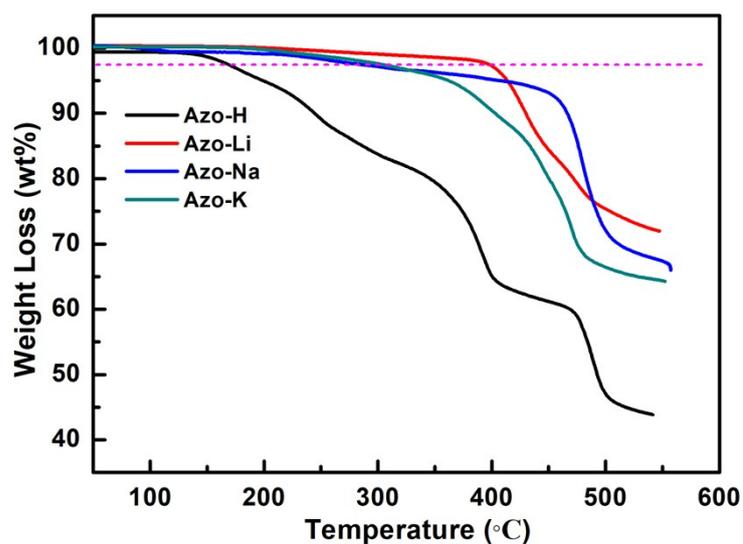


Figure S2. Weight loss for various compounds including Azo-H, Azo-Li, Azo-Na and Azo-K.

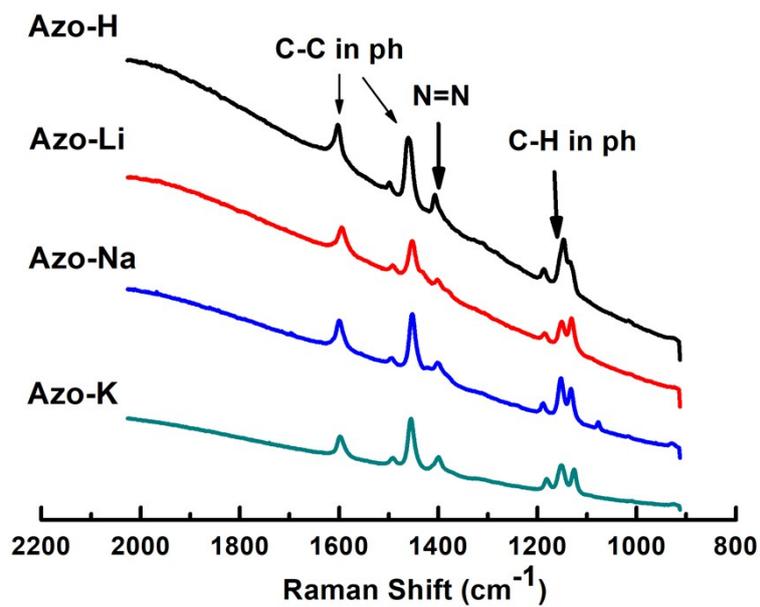


Figure S3. Raman spectra for Azo-H, Azo-Li, Azo-Na and Azo-K at room temperature.

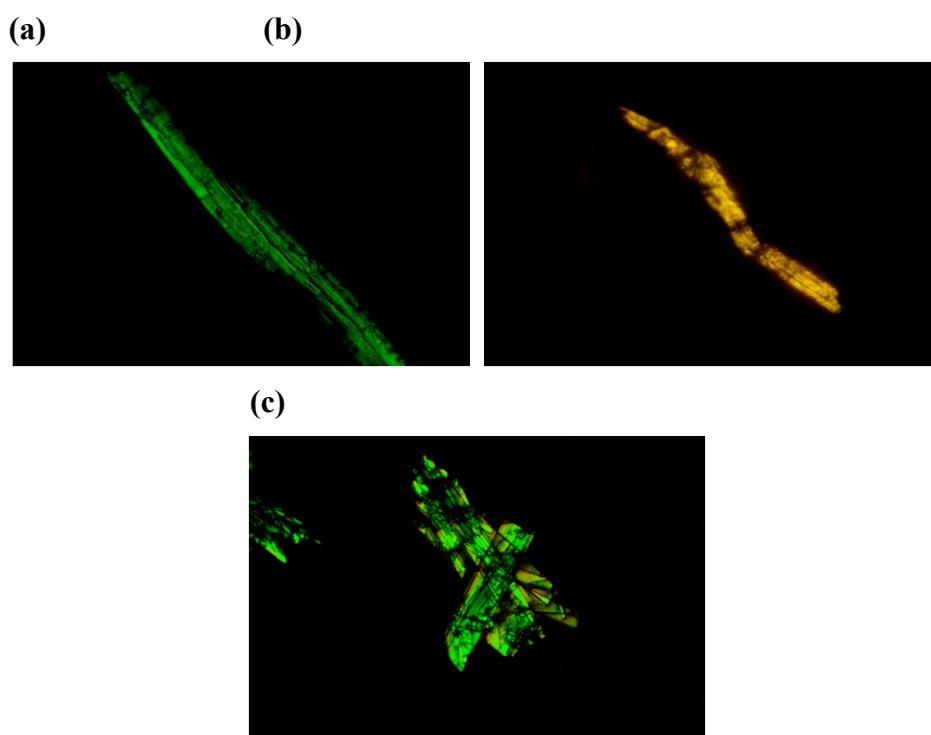


Figure S4. Crystalline textures for Azo-Li (a), Azo-Na (b) and Azo-K (c) observed under polarized optical microscope at room temperature.

4. Tables

Table S1 Mole ratio of *cis*-isomers in aqueous solutions³.

mol ratio of <i>cis</i> -isomers ^a	dark	UV	Visible
Azo-Li	0	62.7%	15.5%
Azo-Na	0	63.2%	11.4%
Azo-K	0	63.9%	16.6%

^a Fraction of the *cis*-isomers under UV light irradiation was calculated by the absorbance change of the band at 331 nm of *trans*-isomers according to Ref. 3. The values of A_t/A_0 represents the fraction of *trans*-azobenzene or the conversion to the *cis*-isomers under UV irradiations, where A_t is absorbance at time t and A_0 is the one at $t=0$.

Table S2 Fitting results for conductivity dependence on time for Azo-Li aqueous solutions.

Equation		$y=A1*\exp(-x/t1)+A2*(-x/t2)+y0$	
		Value	Standard Error
UV	y0	438.16609	1.01975
	A1	-44.26459	7.95752
	t1	0.74376	0.19403
	A2	-56.13746	7.3617
	t2	4.53937	0.65121
Vis	y0	339.90891	1.36E-15
	A1	333403.2025	0.00139
	t1	3.2901	--
	A2	333403.2025	0.00139
	t2	3.2901	--

The values of Adj. R-Square are 0.99517 under UV and 0.9996 under visible light, respectively, suggesting a reasonable fit.

References

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- 2 Y. Huang, H. Kang, G. Li, C. Wang, Y. Huang and R. Liu, *RSC Adv.*, 2013, **3**, 15909–15916.
- 3 H. Tachibana, R. Azumi, T. Nakamura, M. Matsumoto and Y. Kawabata, *Chem. Lett.*, 1992, **73**, 173–176.