

Supporting Information

Anion-dominated Redox Reaction of a SAM of an Alkylthiolated Viologen Bearing a Covalently-attached Intramolecular Sulfonate Group on a Gold Electrode

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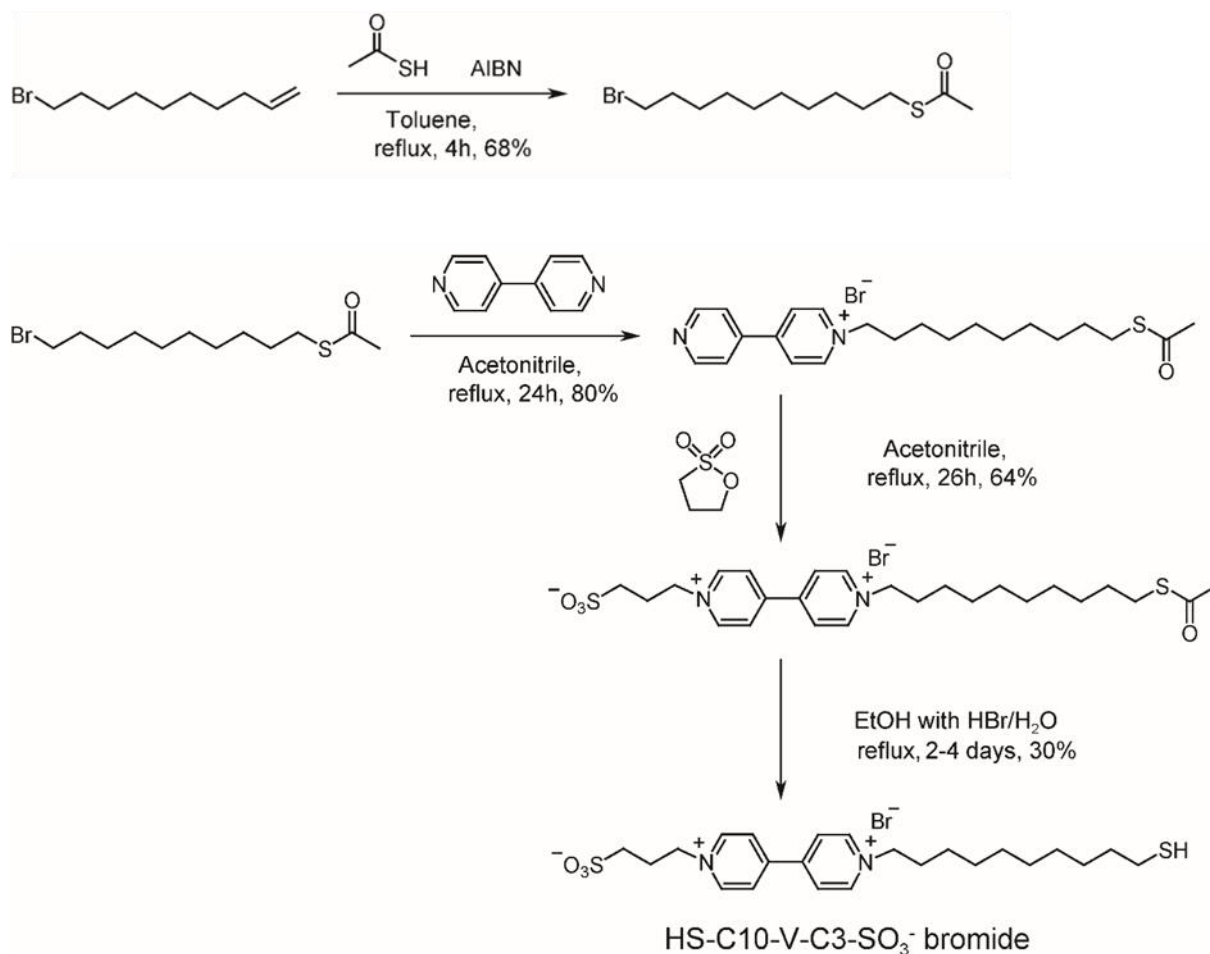
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Scheme S1. Synthetic scheme of 1-(10-mercaptodecyl)-1'-(3-sulfonatopropyl)-4,4'-bipyridinium bromide (HS-C10-V-C3-SO₃⁻ bromide salt). For the ¹H NMR spectrum of the purified product, see Fig. S1.

The above scheme is partially referred to previously reported synthetic methods of viologen thiol derivatives.^{1,2}

References

1. B. B. Narakathua, M. S. Devadas, A. S. G. Reddy, A. Eshkeiti, A. Moorthi, I. R. Fernando, B. P. Miller, G. Ramakrishna, E. Sinn, M. Joyce, M. Rebros, E. Rebrosova, G. Mezei, and M. Z. Atashbar, *Sens. Actuators B Chem.*, **176**, 768 (2013).
2. T. Kawauchi, Y. Oguchi, J. Sawayama, K. Nagai, and T. Iyoda, *Macromolecules*, **48**, 8090 (2015).

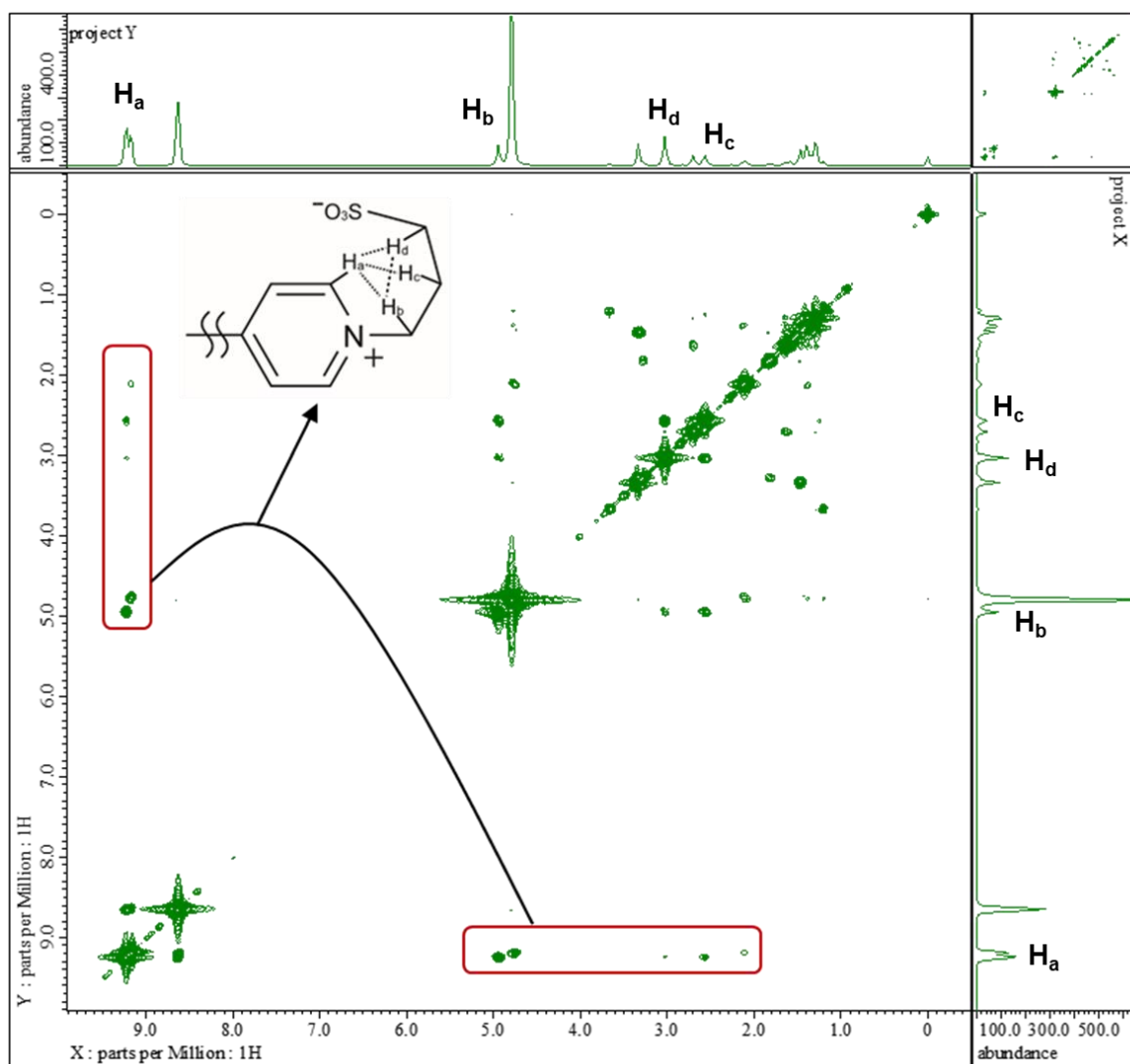


Figure S1. Two-dimensional nuclear Overhauser effect (NOE) spectroscopy of a HS-C10-V-C3-SO₃⁻ bromide.

2D NOE (400 MHz, D₂O-DSS): δ[ppm] = 9.32 (t, 4H), 8.70 (dd, 4H), 4.97 (t, 2H), 4.77 (t, 2H), 2.92 (t, 2H), 2.6 (t, 1H), 2.55 (qi, 2H), 2.11 (m, 2H), 1.10-1.72 (m, 16H).

Figure S1 is consistent with the result of 2D NOE reported by Li *et al.*³ The cross peaks enclosed in the box indicate that the viologen nitrogen site and the sulfonic acid group are approaching each other.

Reference

3. H. Li, H. Fan, B. Hu, L. Hu, G. Chang, and J. Song, *Angew. Chem. Int. Ed.*, **60**, 26971 (2021).