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Supporting Information

Experimental and Theoretical Examination of the Radical Cations Obtained from the Chemical and Electrochemical Oxidation of 5-Aminothiazoles

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Supporting Information

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Cyclic Voltammetry in CH_3CN.

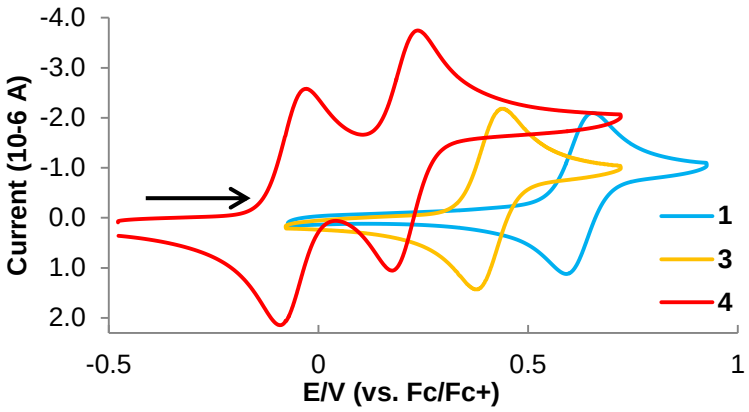


Figure S1. Cyclic voltammogram of **1** (blue), **3** (yellow), and **4** (red) recorded in CH_3CN; 0.1 $_M$ electrolyte [*n*-Bu_4N][ClO_4]; scan rate = 100 mVs^{-1}; reference electrode: Ag/AgCl, counter electrode: Pt, and working electrode: Pt.

Photophysical properties and spectra.

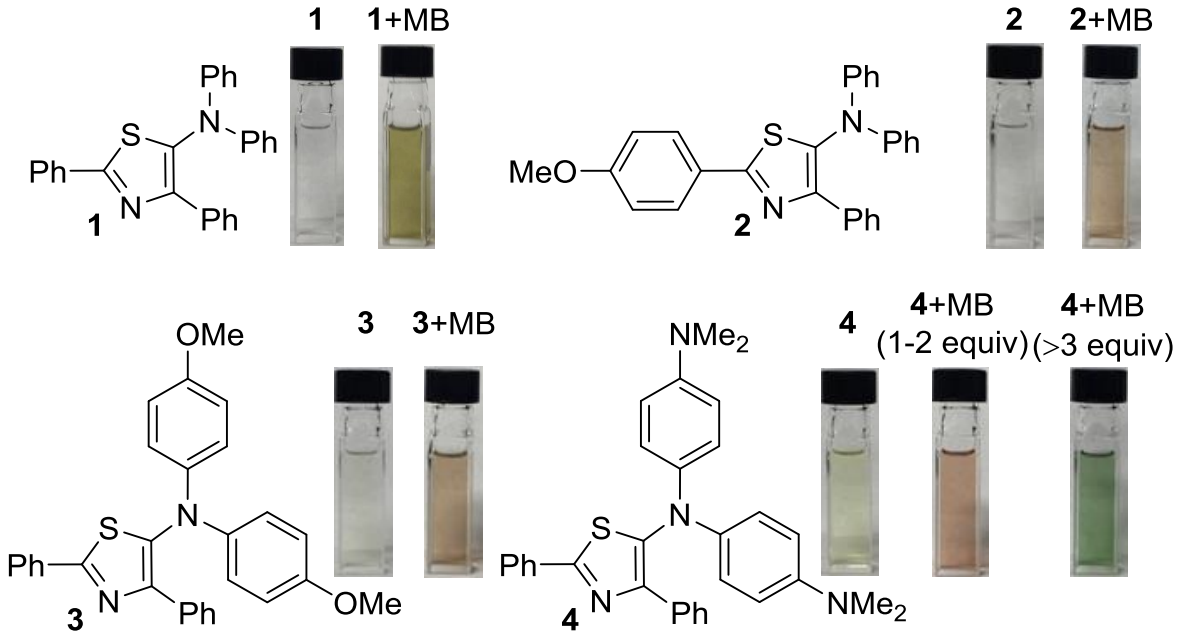


Figure S2. Photographs of solutions of **1**–**4** and **1**+MB–**4**+MB.

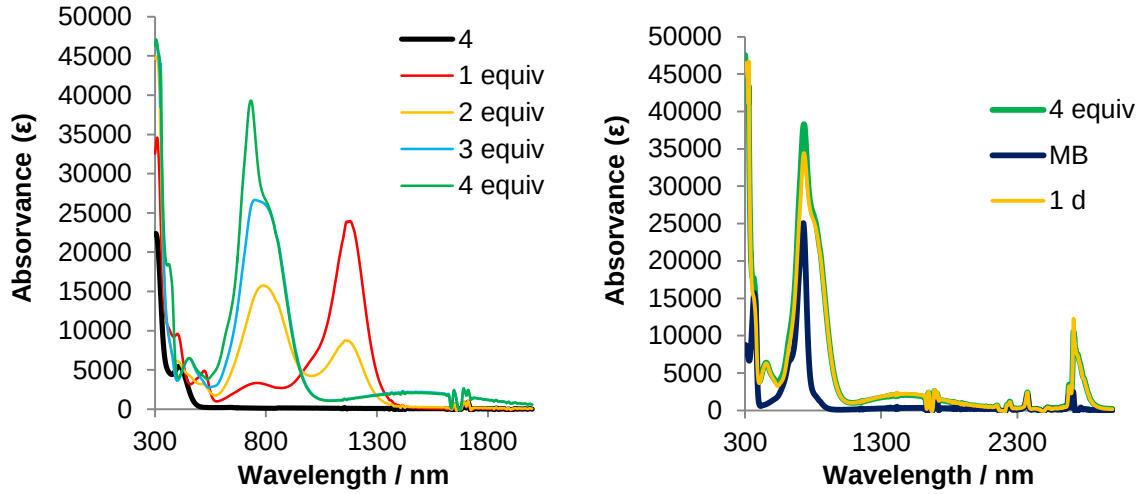


Figure S3. The absorption spectra of **4**, **4** with 1−4 equivalents of MB, only MB and after 1 day of **4** with 4 equivalents of MB in CH_2Cl_2, [**4**] = 1×10^{-4} M.
Absorption of the addition of 4 equivalents of MB almost corresponds to that of MB.

Properties for electrochemical oxidation.

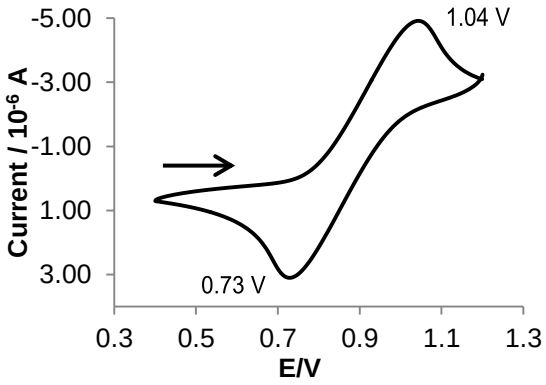


Figure S4. Cyclic voltammograms of **1** recorded in CH_2Cl_2, [**1**] = 1×10^{-4} M, 0.1 M electrolyte [*n*-Bu_4N][ClO_4]; scan rate = 100 mVs^{-1}; reference electrode: Ag/AgCl, counter electrode: Pt, and working electrode: Pt.

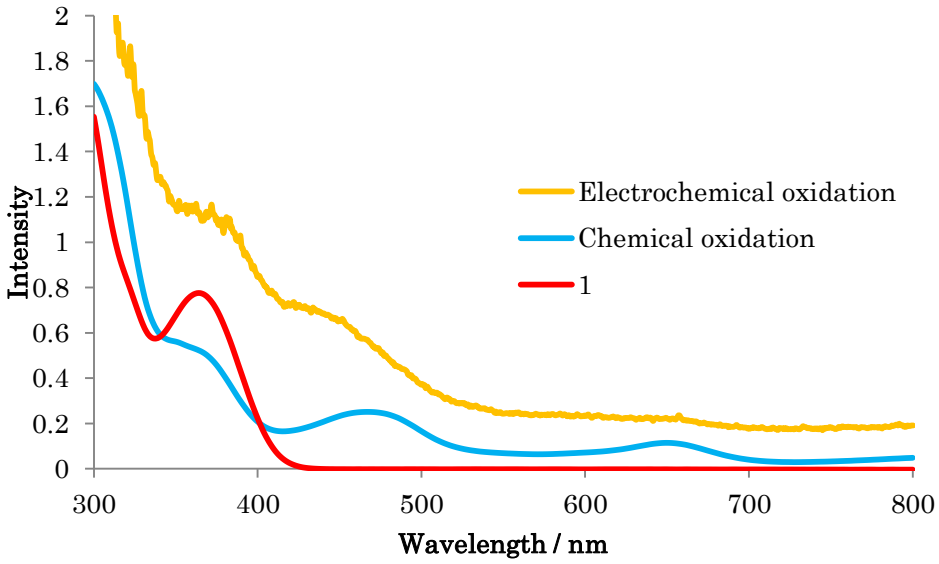
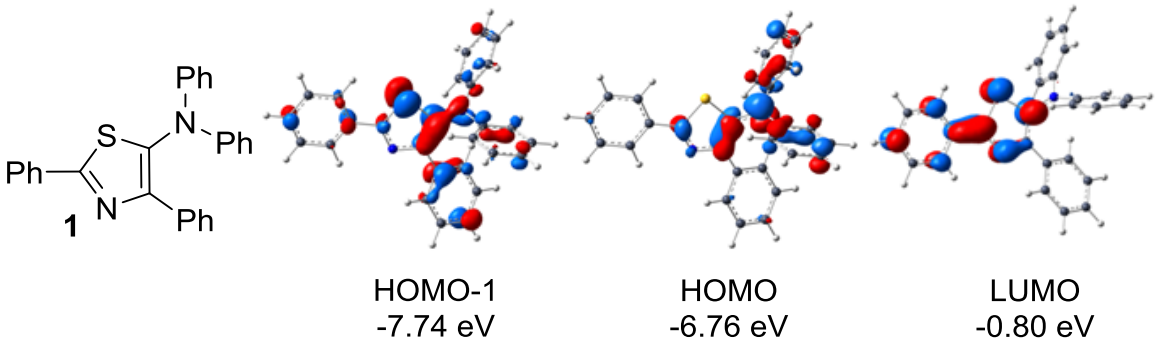


Figure S5. The comparison of absorption spectra of thiazole **1** (blue), electrochemically oxidized **1** (yellow), and chemically oxidized **1** (red) in CH_2Cl_2, [solute] = 1×10^{-4} M.

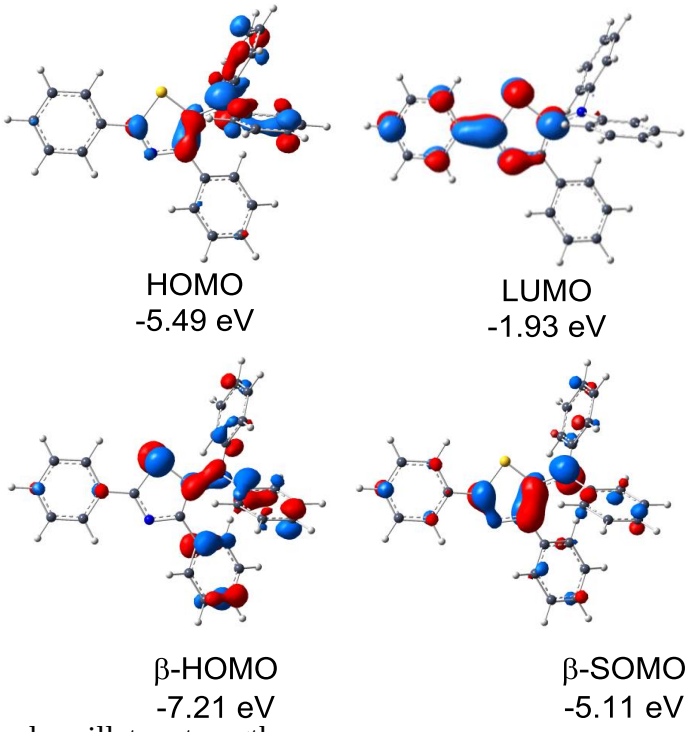
DFT calculations

All the calculations were carried out with the density functional theory (DFT) method as implemented in Gaussian 09 program package.[1] Geometries were optimized at B3LYP level[2] by using the 6-31+G(d) basis set and characterized as minima which have no imaginary frequency. Solvation effect from the CH_2Cl_2 solvent (Eps=8.930) was taken into account through the polarized continuum model (PCM).[3] On the basis of the above optimized geometries, UV/Vis absorption spectra computed with time-dependent (TD) DFT method and *g* tensor along with the hyperfine coupling constants (HFCCs) were calculated at the same level of theory. The spin densities reported here were estimated using Mulliken population analysis.[4]



Excitation energies and oscillator strengths:

349 nm (364 nm in experiment), f=0.389, HOMO→SOMO: 97%



Excitation energies and oscillator strengths:

890 nm (900 nm in experiment), f=0.128, β-HOMO→β-SOMO: 97%

Figure S6. Frontier molecular orbitals for neutral compound of **1** at CAM-B3LYP/6-31+G(d)/PCM(CH_2Cl_2) level (up) and B3LYP/6-31+G(d)/PCM(CH_2Cl_2) level (middle), and radical cation of **1** (bottom) at B3LYP/6-31+G(d)/PCM(CH_2Cl_2) level.

Table S1. DFT calculations of ESR data for cation radical.

Basis set	HFCCs for N atom (A_{iso}_N, mT) and *g* tensor		
	OPT(CH_2Cl_2): B3LYP/6-31+G(d) for all atoms ESR: B3LYP		Exp.
	Gas phase	CH_2Cl_2	CH_2Cl_2
IGLO-III	-	0.54 2.0030 (av.) [2.0021,2.0038, 2.0030][a]	0.72 2.0030
6-31+G(d)	-	0.74 2.0029 (av.) [2.0021, 2.0037, 2.0030]	

[a] For g_{xx}, g_{yy}, g_{zz}.

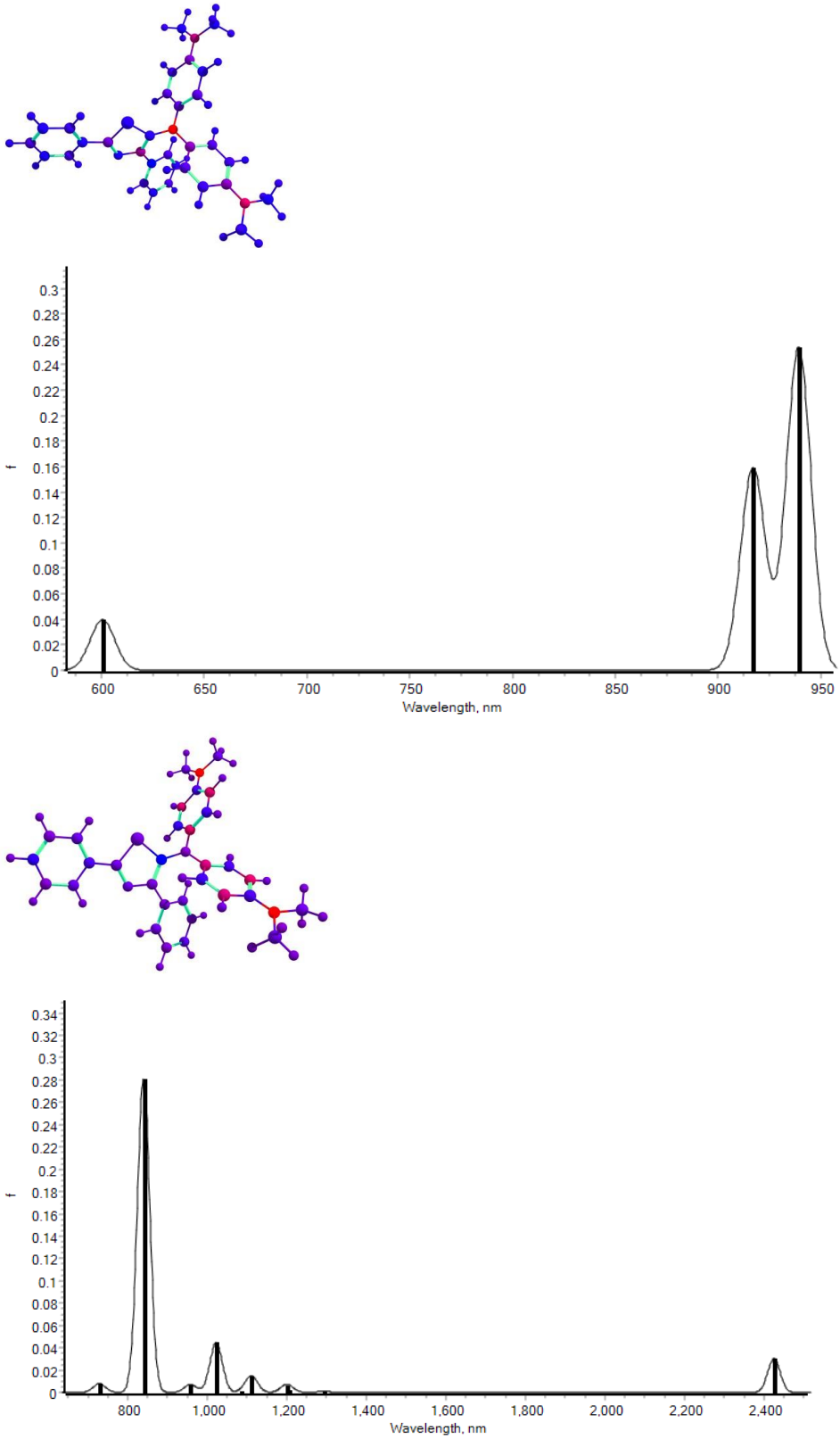


Figure S7. Mulliken spin density maps and absorption spectra for radical cation of **4** at B3LYP/6-31+G(d) level charge+1/doublet (up) and charge+3/doublet (bottom), where positive (red) and negative (blue) spin densities. These images were generated with Chemcraft.

References.

[1] Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2013

[2] a) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098−3100; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648−5652; c) C. T. Lee, W. T. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785−789.

[3] J. Tomasi, B. Mennucci, R. Cammi, *Chem. Rev.* **2005**, *105*, 2999-3094.

[4] R. S. Mulliken, *J. Chem. Phys.* **1955**, *23*, 1833-1840.