

Organometallic dithiolene complex exhibiting an electrochemically initiated hydrogen generation

Mitsushiro Nomura,* Chikako Fujita-Takayama, Takayoshi Yagisawa, Toru Sugiyama, Masatsugu Kajitani

Department of Materials and Life Sciences, Faculty of Science and Technology, Sophia University, 7-1, Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan.

Electronic Supplementary Information

Materials and instrumentation.

Organometallic cobalt dithiolene complexes studied in this work (**1-NH**, **1-NMe**, **1-NMe**, **2-NH**) were prepared by known procedure developed in our research group.¹ Tetraethylammonium perchlorate (TEAP) was provided from Nacalai Tesque, Inc. Ferrocene was obtained from Tokyo Chemical Industry Co., Ltd. UV-Vis spectra were measured in 5.0×10^{-5} MeCN solutions of complexes and were recorded on a Hitachi model UV-2500PC.

CV Measurements.

All electrochemical measurements were performed under an argon atmosphere. MeCN as a solvent for electrochemical measurements (HPLC grade) were given from Wako Chemicals, and further dried over molecular sieve 4A before use. A platinum wire served as a counter electrode, and the reference electrode Ag/AgNO₃ was corrected for junction potentials by being referenced internally to the ferrocene/ferrocenium (Fc/Fc⁺) couple. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode. The Model CV-50W instrument from BAS Co. was used for cyclic voltammetry (CV) measurements. CVs were measured in 1 mmol·dm⁻³ MeCN solutions of complexes containing 0.1 mol·dm⁻³ tetraethylammonium perchlorate (TEAP) at 25 °C.

Spectroelectrochemical measurement.

The spectroelectrochemical data were obtained during bulk electrolysis for 1 mmol·dm⁻³ MeCN solutions of complexes containing 0.1 mol·dm⁻³ TEAP at 25 °C in an optically transparent thin-layer electrode (OTTLE, thin-layer thickness = 0.4 mm)² cell. Measurements were made with MCPD-7000 rapid scan spectrometer and MC-2530 of Otsuka Electronics Co., Ltd. The working electrode was stationary platinum mesh in thin-layer form. A CV measurement using a thin-layer cell was performed by using the same OTTLE cell above.

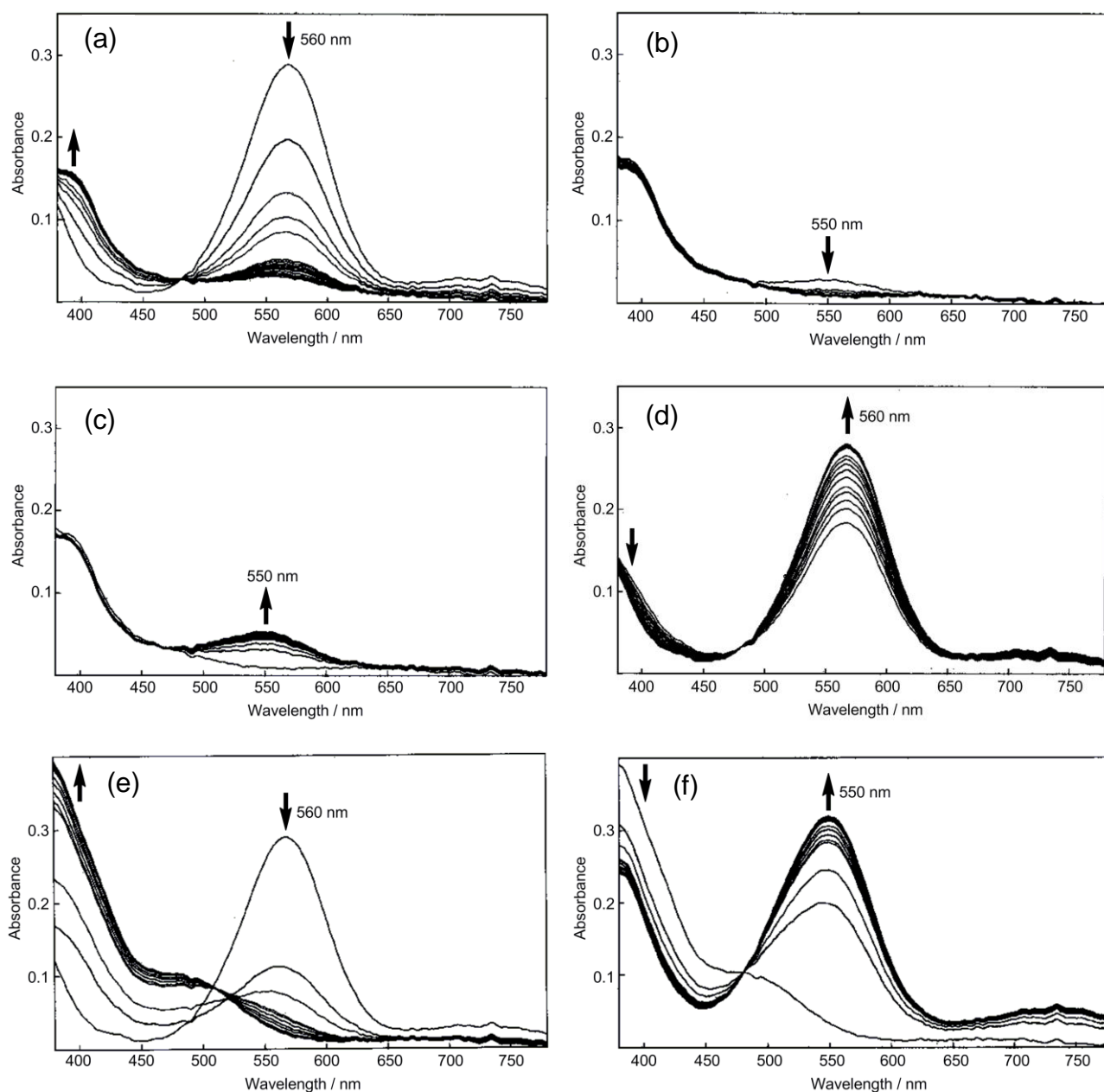


Fig. S1. UV-vis spectral changes of **1-NH** during (a) reduction (-0.2 V to -1.2 V, sampling time 30 s, sampling interval 2 s), (b) reduction (-1.2 V to -1.6 V), (c) reoxidation (-1.6 V to -1.2 V), (d) reoxidation (-1.2 V to -0.2 V), (e) reduction (-0.2 V to -2.2 V) and (f) reoxidation (-2.2 V to -1.2 V). Figs. S1(a), S1(b) and S1(f) are adapted from Fig. 2 in the main text.

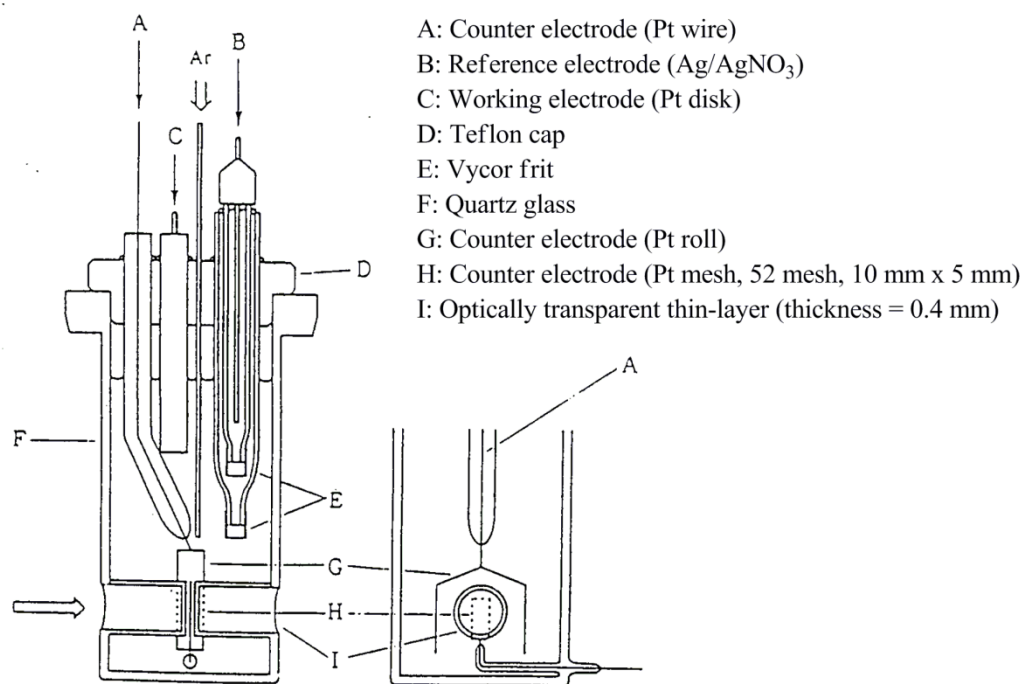


Fig. S2. Optically transparent thin-layer electrode (OTTLE) cell used in this work.

Density functional theory (DFT) calculation.

Geometries of **1-NH** and **1-N⁻** were optimized with no constraint using the Gaussian 03 package³ and the hybrid functional B3LYP.⁴ The standard 3-21G* basis⁵ set was used for H, C and S together with the LanL2DZ for Co. Energy minima were confirmed by frequencies analysis.

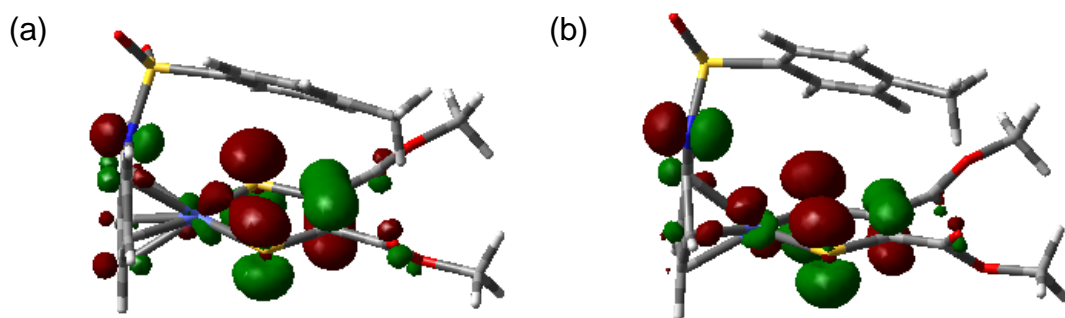


Fig. S3. (a) Distribution of highest occupied molecular orbital (HOMO) of **1-NH** and (b) HOMO of **1-N⁻** (isovalue = 0.05).

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