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Electronic Supplementary Information

Incorporation of Cationic Electron Donor of Ni-pyridyl-tetrathiafulvalene with Anionic Electron Acceptor of Polyoxometalate

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Contents

1. TG diagram

The solvent number of CH_3CN molecules was determined by TG-DTA measurement using a Rigaku Thermo Plus TG8120 with a scanning rate of 10 K min^{-1} under N_2 flow. These measurements showed an about 2.6 % of weight loss by increasing of the temperature up to 373 K, which corresponds about three CH_3CN molecules in crystal.

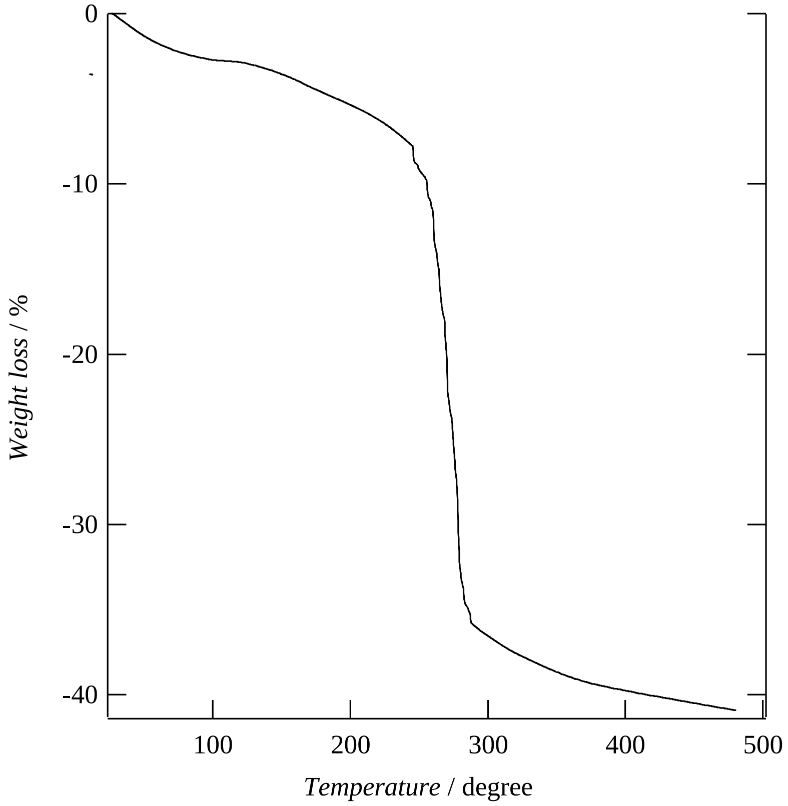


Figure S1. TG diagram of crystalline salt of **1**.

2. Formation and redox activity of cationic donor of {TTFPy-Ni}

In MeCN. The band observed at 425 nm corresponds with the HOMO–LUMO transition of TTFPy in MeCN. On increasing the Ni ion concentration, a new band at 460 nm was appeared gradually with an isosbestic point at 437 nm, showing the formation of {TTFPy-Ni} complex cations.

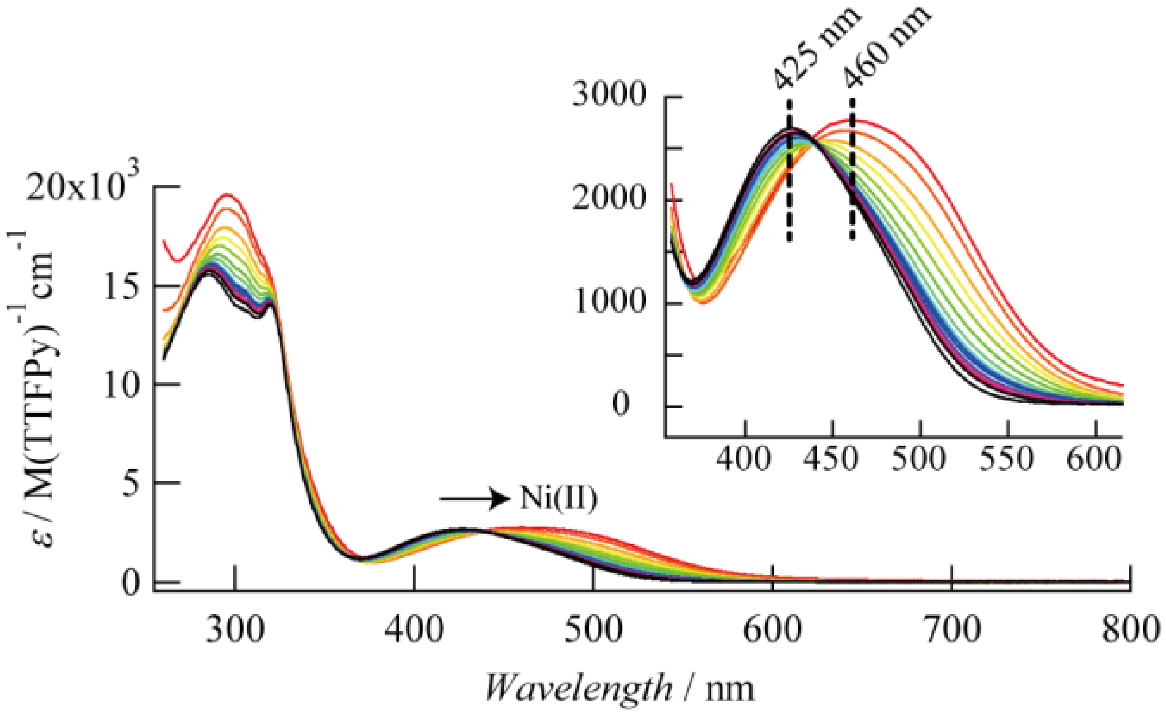


Fig. S2 UV–vis spectra of TTFPy (1 mM) with $Ni(NO_3)_2$ in MeCN. Molar ratio varied from Ni:TTFPy = 0.1:1 (blue side) to 8:1 (red side).

In DMSO. By contrast, a similar experiment in DMSO solution did not show any shift of the HOMO-LUMO transition, suggesting that the Ni ions were coordinated only by DMSO molecules. Band at 435 nm is corresponded with HOMO-LUMO transition of TTFPy molecule. λ_{max}(DMSO)/nm 435(ε/dm^3 mol^{-1} cm^{-1} 3 100). By contrast in MeCN solution shown in main text, a similar experiment in DMSO solution did not show any shift of the HOMO-LUMO transition, suggesting that the Ni ions were coordinated only by DMSO molecules. Thus, the coordination abilities of DMSO, TTFPy and MeCN molecules with the Ni ion are assumed to decrease in this order. A single crystal of **1** was obtained from the mixed solvent system of MeCN/DMSO (>11:1), in which the cationic $[Ni^{II}(DMSO)_5(TTFPy)]^{2+}$ unit is preferentially formed instead of $[Ni^{II}(DMSO)_5(MeCN)]^{2+}$.

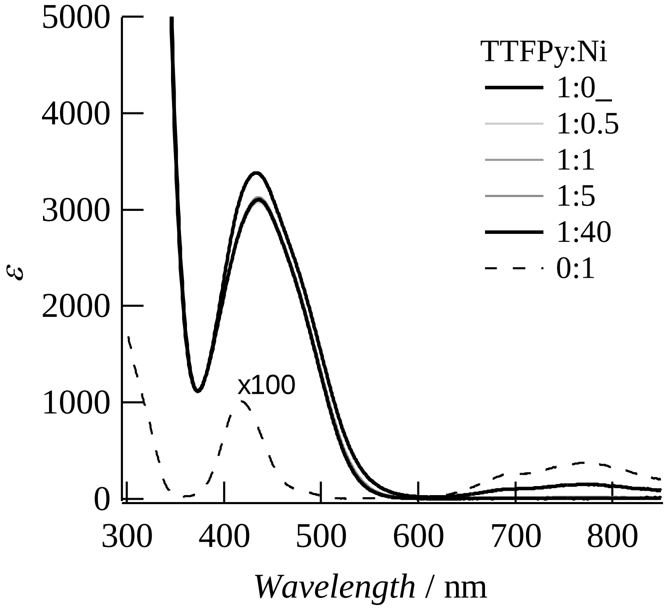


Figure S2-2. UV-vis spectra of TTFPy (1.0 mM) in DMSO under titration of Ni ion

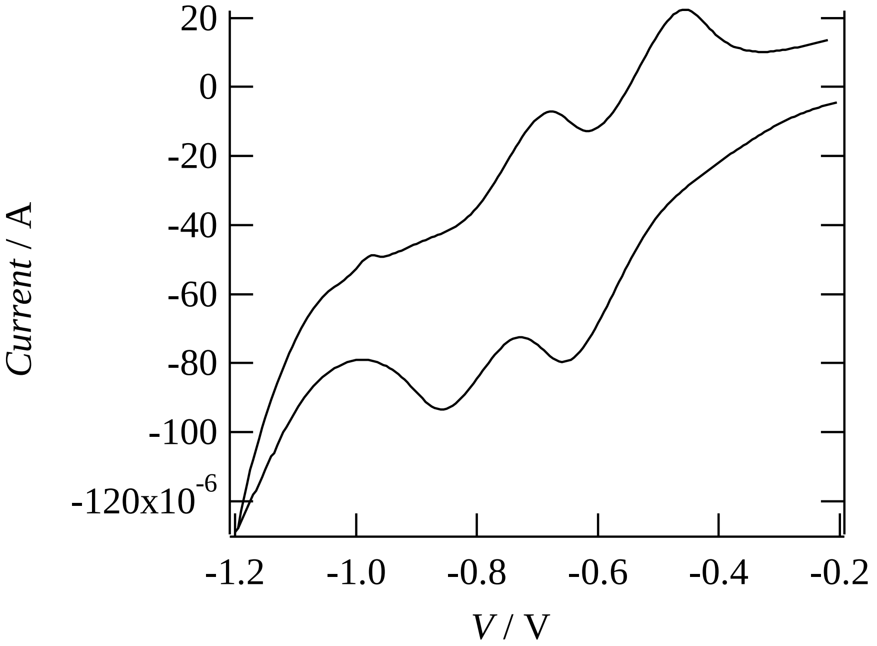


Figure S2-3. CV data of $[SiW_{12}O_{40}]^{4-}$ anion in methanol at 40 mM with 0.1 M n-Bu_4NClO_4 as a supporting electrolyte, platinum electrodes (working- and counter-electrodes) and a Ag/AgCl electrode as a reference with a scan rate of 50 mVs^{-1}.

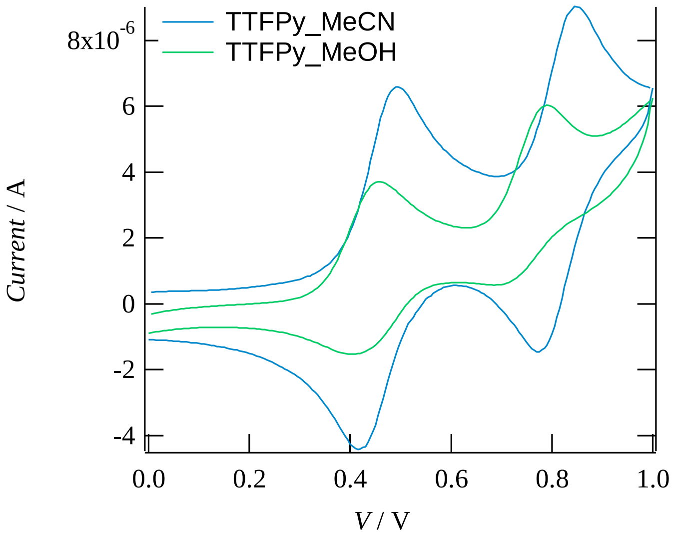


Figure S2-4 CV data of TTFPy in methanol at 1.0 mM with electrolyte of *n*-Bu_4NClO_4 (0.1 M) with 0.1 M *n*-Bu_4NClO_4 as a supporting electrolyte, platinum electrodes (working- and counter-electrodes) and a Ag/AgCl electrode as a reference with a scan rate of 50 mVs^{-1}.

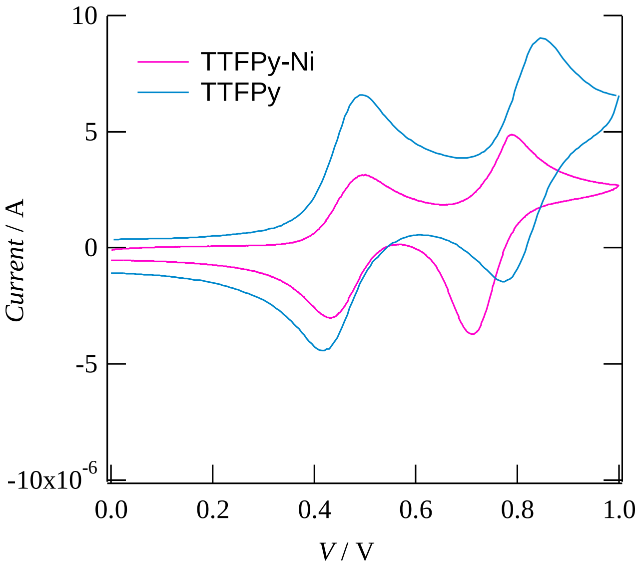


Figure S2-5 CV data of TTFPy and {TTFPy-Ni} (Ni:TTFPy = 10:1) in acetonitrile at 1.0 mM with electrolyte of Bu_4NClO_4 at 0.1 M (at 50 mV/s). Their first half wave oxidation potentials were observed at similar potential at 0.464 V and 0.450 V, respectively under the condition of oxidation by one electron. However, they did show different redox process at second redox process. The second half wave potentials were observed at 0.810 V and 0.749 V on TTFPy and {TTFPy-Ni}, respectively. The negative shift would be associated with electron transfer between TTFPy and Ni^{II}, where oxidation potential for $Ni^{II/III}$ was reported around at 0.8-1.0 V vs Ag/AgCl depended on ligand coordinated with Ni ion (for example see; I. R. Whittall, M. P. Cifuentes, M. G. Humphrey, B.

Luther-Davies, M. Samoc, S. Houbrechts, A. Persoons, G. A. Heath, and D. Bogsányi, *Organometallics* 1997, 16, 2631-2637.).

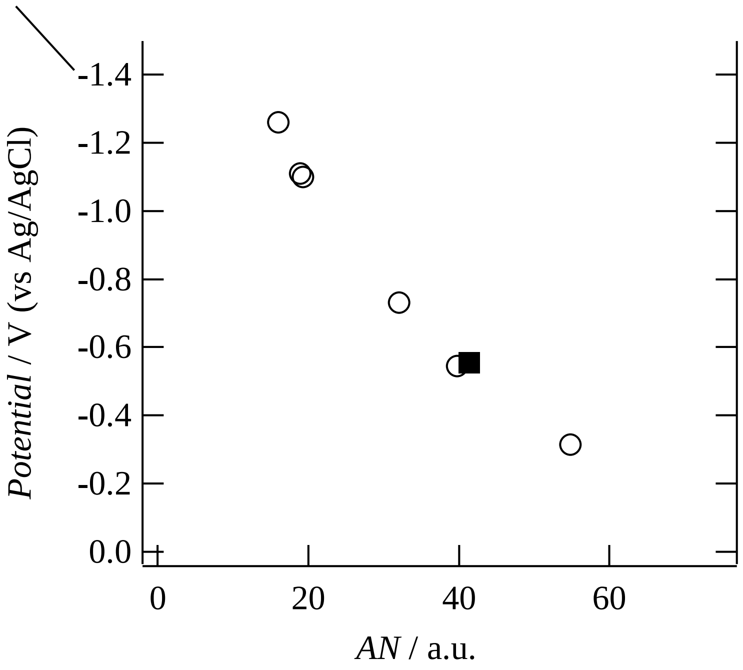


Figure S2-6. Plots of first half wave potentials of $[SiW_{12}O_{40}]^{4-}$ with solvent acceptor number (*AN*) in which measurements were performed. The black square represents that in methanol and it fitted on the linear plot reported before (see ref 18 in main text).

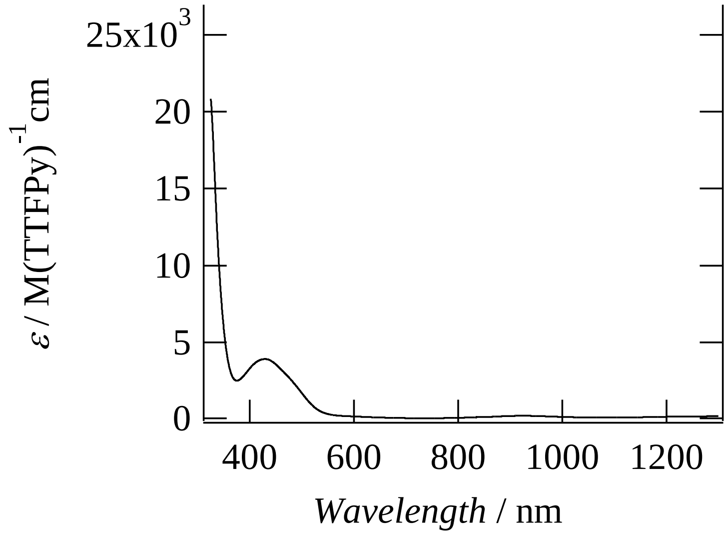


Figure S2-7. UV-vis-NIR spectrum of **1** dissolved in DMSO (1.3 mM) . Band at 427 nm is corresponded with HOMO-LUMO transition of TTFPy molecule where Ni ion is not coordinated with TTFPy. λ_{max}(DMSO)/nm 429 (ε/dm^3 mol^{-1} cm^{-1} 3 900)

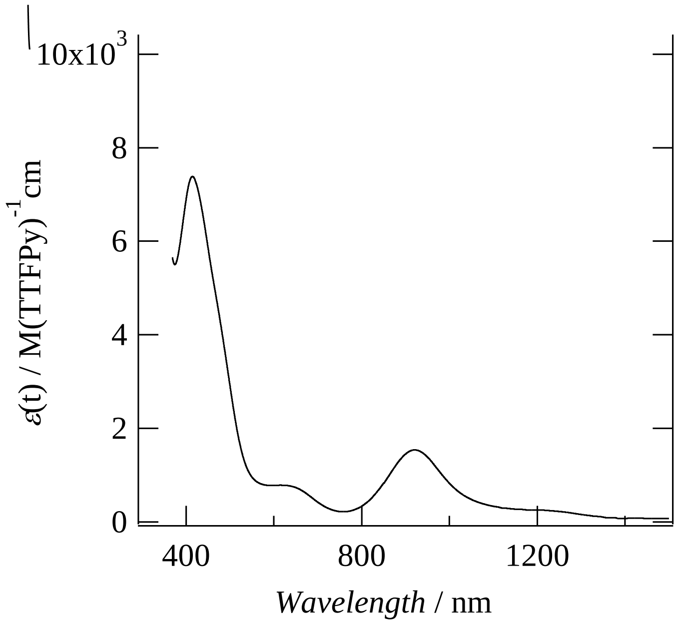
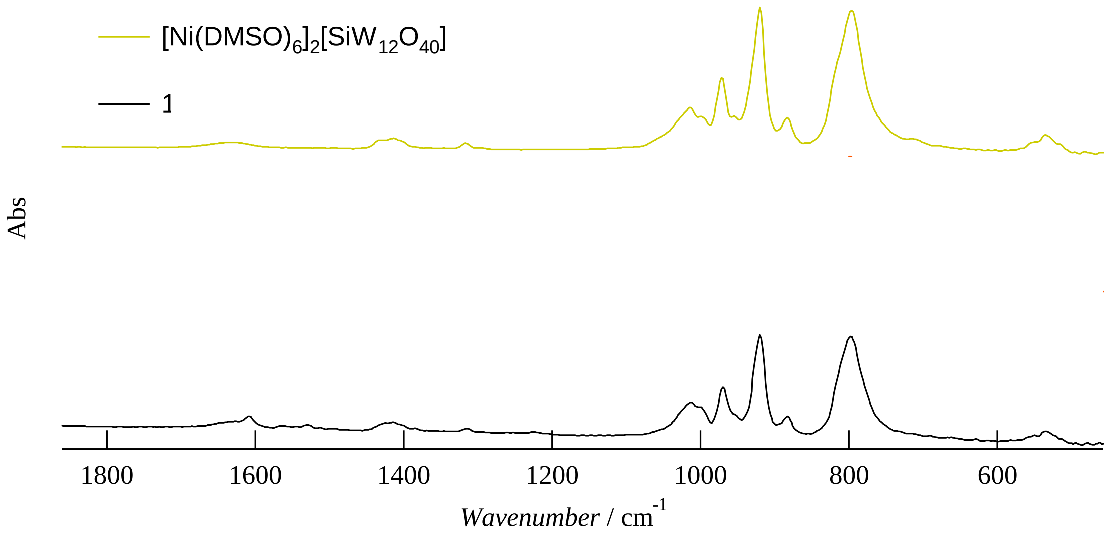


Figure S2-8. UV-vis-NIR spectrum of DMSO solution of **1’**

3. IR spectra



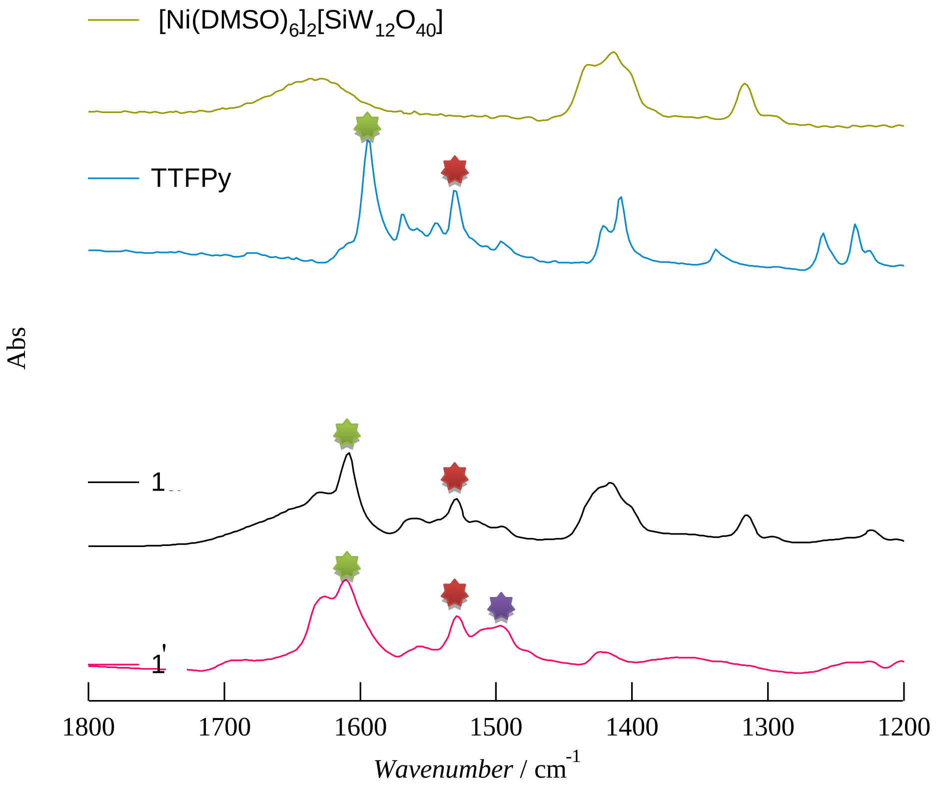


Figure S3. IR spectra of TTFPy, **1**, **1'** (20 h of immersing in methanol), [Ni(DMSO)$_6$]$_2$[SiW$_{12}$O$_{40}$] and TTFPy. The peak at 1608 cm^{-1} in **1** was associated with vibration mode originated from pyridyl moiety in TTFPy (*green stars*). The shift from 1595 cm^{-1} in TTFPy indicated coordination with Ni. The peak around at 1531 cm^{-1} in TTFPy, **1** was assigned to C=C vibration mode of TTF (*red stars*; R. Bozio, A. Girlando and D. Pecile, *Chem. Phys. Lett.*, 1977, **52**, 503-508), and this peak was sensitive against oxidation state of TTF moiety. Upon oxidation of TTF to TTF^+, it shows shift from 1530 cm^{-1} to 1478 cm^{-1} (R. Bozio, I. Zanon, A. Girlando, and C. Pecile, *J. Chem. Phys*., 1979, **71**, 2282-2293). Compound **1** showed clear growth of peak at 1495 cm^{-1} (*purple star*) by immersing in methanol (compound **1'**), indicating that TTFPy was oxidized to TTF^+Py.

4. ESR spectra

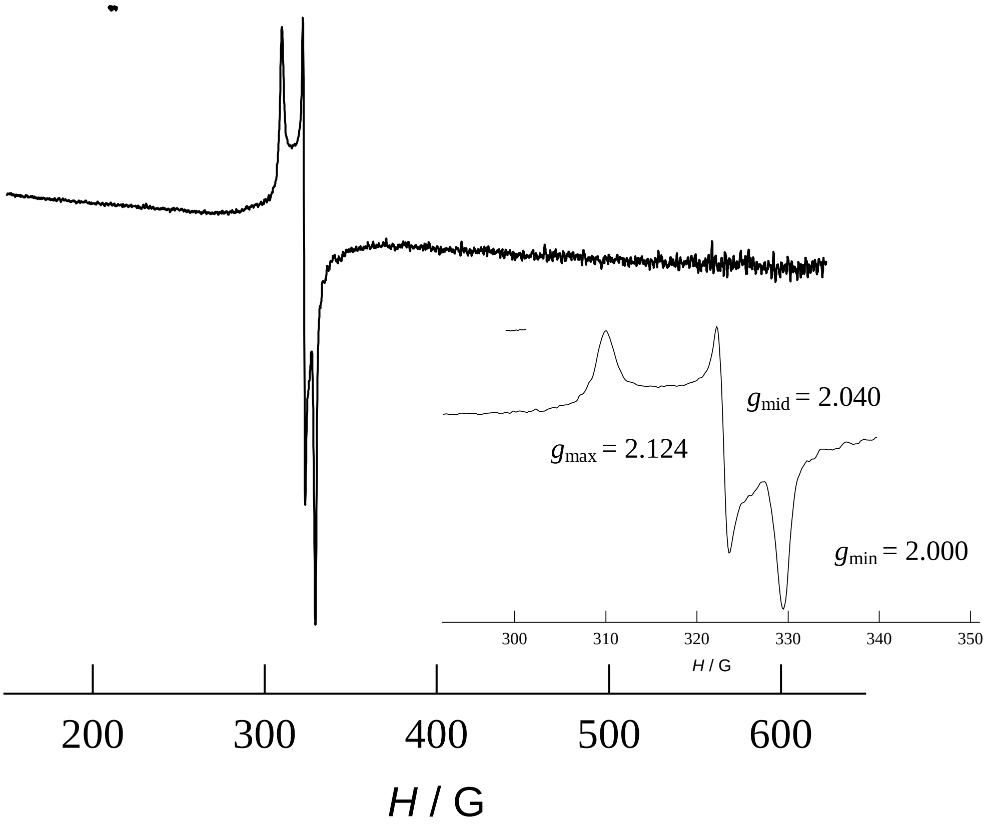


Figure S4. ESR spectrum of polycrystalline sample of **1'** frozen in MeOH was characterized at 77 K with 9.454 GHz of frequency. The spectrum of TTF^+Py radical was quantitatively corresponded with that of TTF^+ radical (see ref 20 in main text). The signals originated from W^V is unclear. This would be due to re-oxidation by air and/or concentration of W^V specie is too low. It has been reported that successful ESR measurement of $[SiW^VW^{VI}_{11}O_{40}]^{5-}$ specie were performed using high concentrated solution (J. Livage et al, *J. Am. Chem. Soc*, 1983, **105**, 6817).