

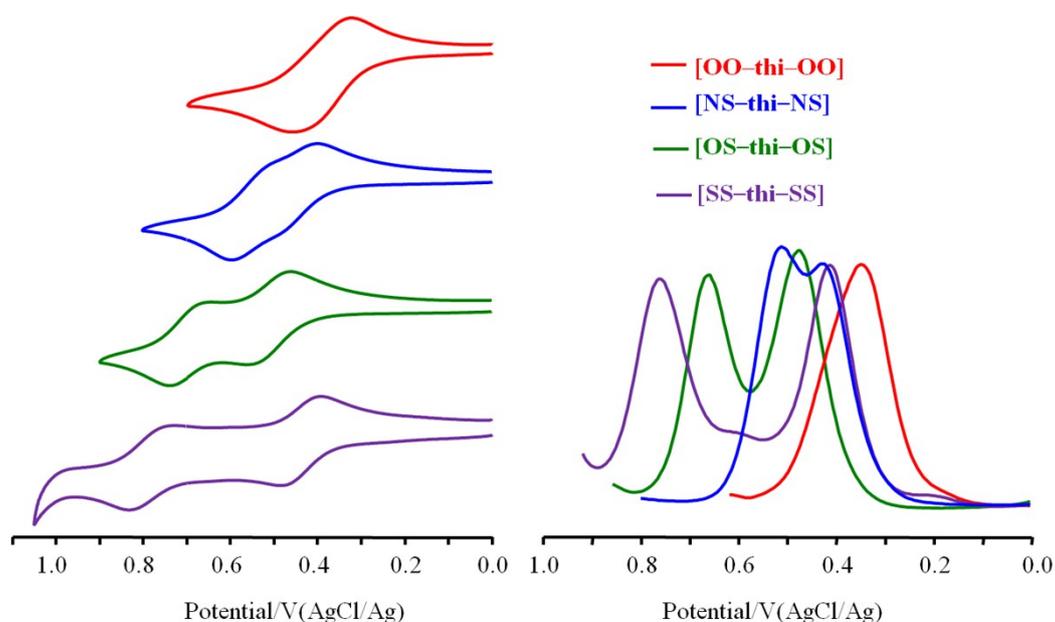
## Optically Probing the Localized to Delocalized Transition in Mo<sub>2</sub>–Mo<sub>2</sub> Mixed-valence Systems

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### Supporting Information

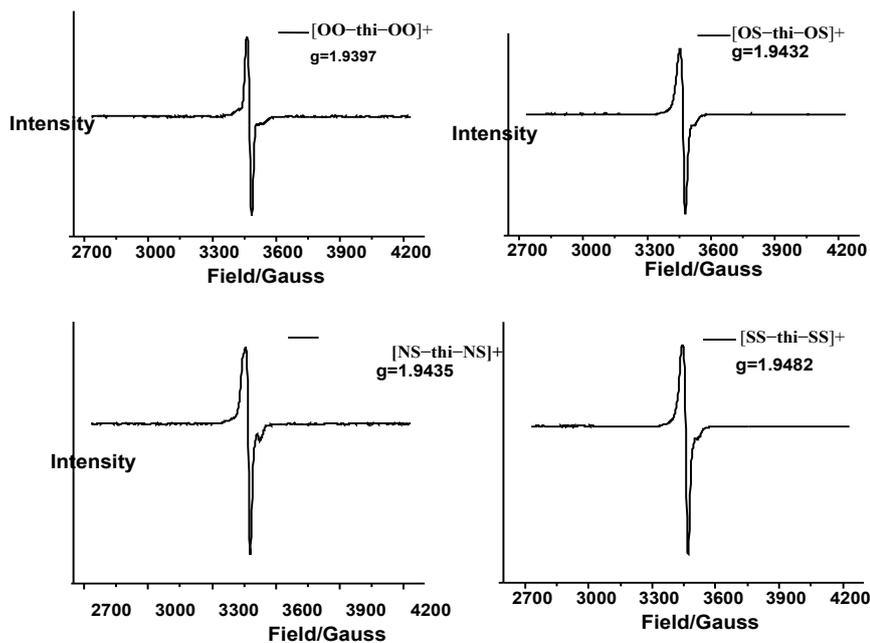
1. **Figure S1.** CVs and DPVs for [OO–thi–OO], [NS–thi–NS], [OS–thi–OS] and [SS–thi–SS].
2. **Table S1.** Electrochemistry data for [OO–thi–OO], [NS–thi–NS], [OS–thi–OS] and [SS–thi–SS].
3. **Figure S2.** EPR Spectra of the [OO–thi–OO]<sup>+</sup>, [NS–thi–NS]<sup>+</sup>, [OS–thi–OS]<sup>+</sup> and [SS–thi–SS]<sup>+</sup>.
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10. **Experimental section**
11. **<sup>1</sup>H NMR characterization (Figure S8-S11).**



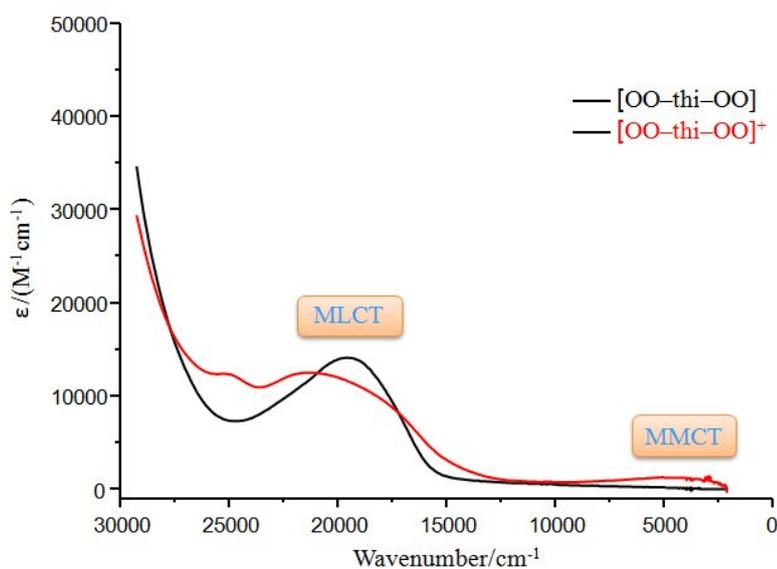
**Figure S1.** CVs (left) and DPVs (right) for [OO–thi–OO], [NS–thi–NS], [OS–thi–OS] and [SS–thi–SS].

**Table S1.** Electrochemistry data for [OO-thi-OO], [NS-thi-NS], [OS-thi-OS] and [SS-thi-SS].

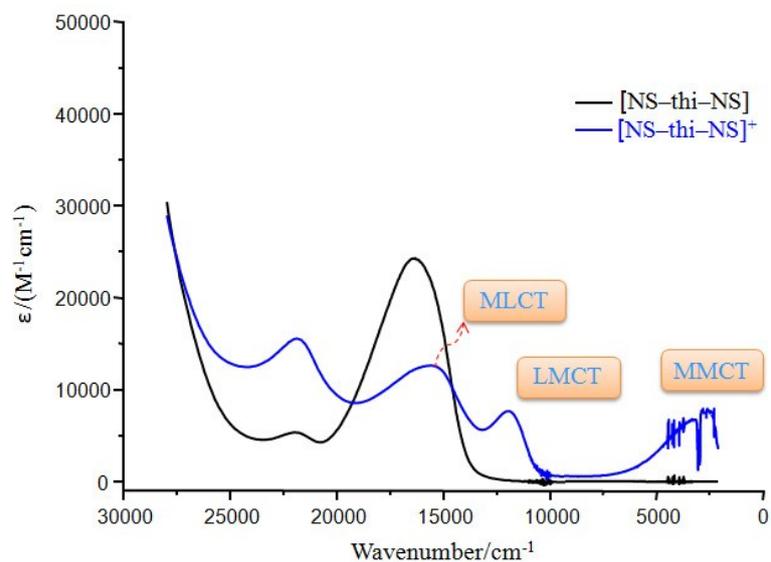
compd	$E_{1/2}(1)$ (mV)	$E_{1/2}(2)$ (mV)	$\Delta E_{1/2}$ (mV)
[OO-thi-OO]	337	413	76
[NS-thi-NS]	407	525	118
[OS-thi-OS]	478	662	184
[SS-thi-SS]	416	764	348



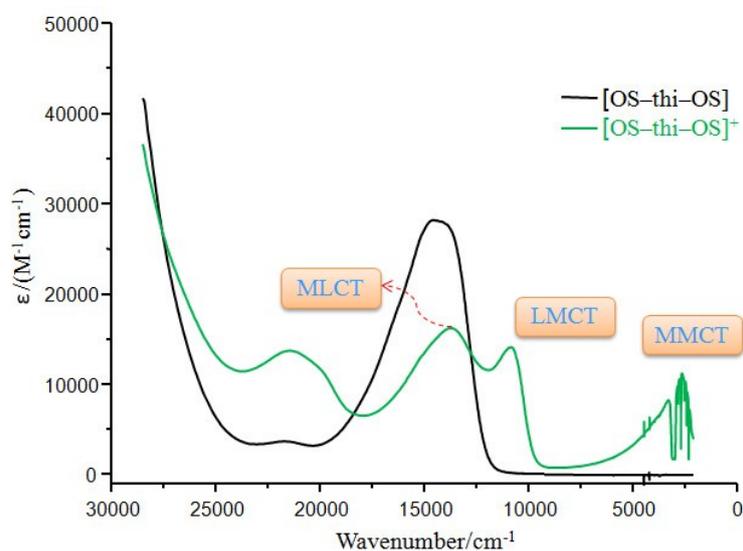
**Figure S2.** EPR Spectra of the [OO-thi-OO]<sup>+</sup>, [NS-thi-NS]<sup>+</sup>, [OS-thi-OS]<sup>+</sup> and [SS-thi-SS]<sup>+</sup>. EPR spectra of the radical cations were generated by single oxidation of the neutral compounds using one equivalent of ferrocenium.



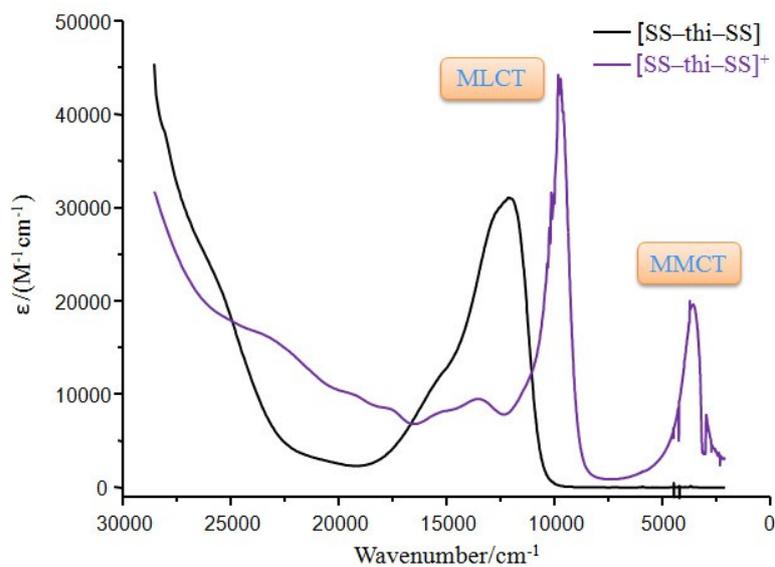
**Figure S3.** UV-Vis-Near-IR spectra for [OO-thi-OO] (black) and [OO-thi-OO]<sup>+</sup> (red) in CH<sub>2</sub>Cl<sub>2</sub>.



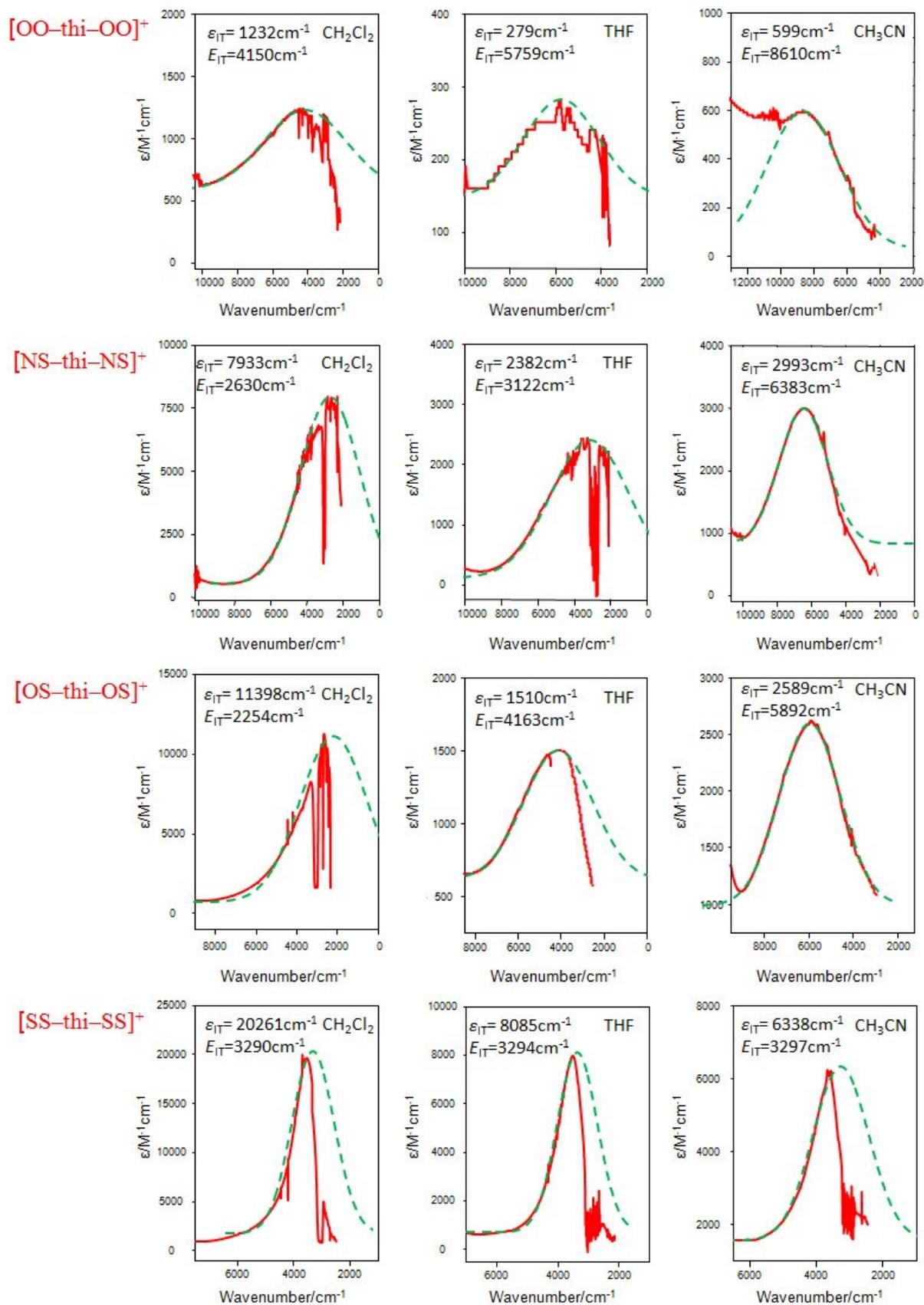
**Figure S4.** UV-Vis-Near-IR spectra for [NS-thi-NS] (black) and [NS-thi-NS]<sup>+</sup> (blue) in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S5.** UV-Vis-Near-IR spectra for [OS-thi-OS] (black) and [OS-thi-OS]<sup>+</sup> (green) in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S6.** UV-Vis-Near-IR spectra for [SS-thi-SS] (black) and [SS-thi-SS]<sup>+</sup> (purple) in CH<sub>2</sub>Cl<sub>2</sub>.



**Figure S7.** The IVCT absorption bands for the mixed-valence complexes [OO-thi-OO]<sup>+</sup>, [NS-thi-NS]<sup>+</sup>, [OS-thi-OS]<sup>+</sup> and [SS-thi-SS]<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub>, THF and CH<sub>3</sub>CN.

**Table S2.** Calculations of the electronic coupling matrix elements and the cut-off effects of the IVCT bands for the MV systems.

compd	$E_{IT}$	$\epsilon_{IT}$	$H_{ab}$	$\Delta v_{1/2(\text{exp})}$	$\Delta v_{1/2}^\circ$	Cut-off
[OO–thi–OO] <sup>+</sup>	4150	1232	561	3998	5404	26%
[NS–thi–NS] <sup>+</sup>	2630	7933	892	2480	3940	37%
[OS–thi–OS] <sup>+</sup>	2254	11398	1127	2009	3931	49%
[SS–thi–SS] <sup>+</sup>	3290	20261	1646	1266	1741	27%

For each of the complexes, the “cut-off” was calculated by comparison of the observed bandwidth ( $\Delta v_{1/2(\text{exp})}$ ) with the calculated value ( $\Delta v_{1/2}^\circ$ ) from  $\Delta v_{1/2}^\circ = (2310 v_{\text{max}})^{1/2}$  ( $v_{\text{max}} = E_{IT}$ ) at the high temperature limit, that is,

$$\text{cut-off} = (1 - \Delta v_{1/2(\text{exp})} / \Delta v_{1/2}^\circ) \times 100\%$$

For [OO–thi–OO]<sup>+</sup> and [NS–thi–NS]<sup>+</sup>,  $H_{ab}$  was calculated from the Hush expression,

$$H_{ab} = 0.0206(\epsilon_{IT}\Delta v_{1/2(\text{exp})}E_{IT})^{1/2}/r_{ab},$$

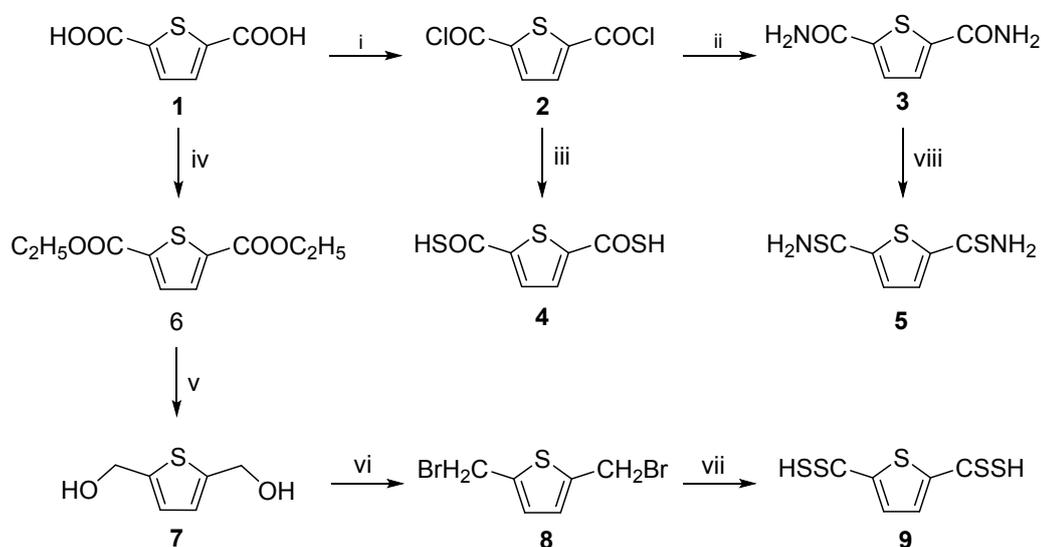
where  $r_{ab}$  was determined to be 5.25 Å from the geometrical length of the thienylene group “–C<sub>4</sub>H<sub>2</sub>S–” according to our previous work. (see for example, C. Y. Liu, X. Xiao, M. Meng, Y. Zhang and M. J. Han, *J. Phys. Chem. C*, **2013**, *117*, 19859–19865, X. Xiao, M. Meng, H. Lei, C. Y. Liu, *J. Phys. Chem. C* **2014**, *118*, 8308–8315).

## Experimental section

**Materials and Methods.** All manipulations were performed in a nitrogen filled glovebox or by using standard Schlenk-line techniques. All solvents were purified by freshly distillation over appropriate drying agents under nitrogen. HDAniF<sup>1</sup> and Mo<sub>2</sub>(DAniF)<sub>3</sub>(O<sub>2</sub>CCH<sub>3</sub>) were synthesized according to literature methods.<sup>2</sup>

**Physical measurements.** Elemental analyses were determined with an Elementar Vario EL elemental analyzer. UV/Vis spectra were measured with a Shimadzu UV-3600 UV/Vis/NIR spectrophotometer in CH<sub>2</sub>Cl<sub>2</sub> solution. <sup>1</sup>H NMR spectra were recorded with a Bruker Avance III 300 spectrometer. CVs and differential pulse voltammograms (DPVs) were recorded with a CH Instruments model CHI660D electrochemical analyzer in 0.10 M CH<sub>2</sub>Cl<sub>2</sub> solution of n-Bu<sub>4</sub>NPF<sub>6</sub>, with Pt working and auxiliary electrodes, an Ag/AgCl reference electrode, and a scan rate of 100 mV s<sup>-1</sup>.

### Syntheses of the three bridging ligands.



**Scheme S1** i)  $\text{SOCl}_2$ , DMF, 90 °C reflux, 12 h; ii)  $\text{NH}_3 \cdot \text{H}_2\text{O}$ , THF, 0 °C, 1 h; iii) a)  $\text{CH}_3\text{CSNH}_2$ , benzene, 35 °C, 4 h; b) NaOH, HCl; iv):  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{H}_2\text{SO}_4$ , Reflux, 72 h; v) a)  $\text{LiAlH}_4$ , THF, 0 °C 0.5 h; b) 80 °C reflux, 12 h; vi) Ether, Anaerobic, 48% HBr; vii) a) S,  $\text{NaOCH}_3$ ,  $\text{CH}_3\text{OH}$ , 70 °C reflux, 12 h; b) HCl; viii) Lawson reagent, toluene, reflux, 6h.

**Preparation of 2,5-thiophenedithioamide (5).** A mixture of 2,5-thiophenedicarboxylic acid (**1**) (1.72 g, 10.00 mmol) and thionyl chloride (25 mL) was refluxed, in the presence of catalytic amount of DMF, at 90 °C for 12 h. The resultant light-green solution was cooled to room temperature and the excess thionyl chloride was removed under reduced pressure. The residue was washed with hexane (3×15 mL) and dried by vacuum. Yield: 1.85 g (89%). This material (**2**) was used for preparation of **3** without further purification.

To a solution prepared by dissolving **2** (1.7 g, 8.2 mmol) in 30 mL of THF was added dropwise 5 mL of aqueous ammonia (25%). With stirring, the reaction was kept in the ice bath for one hour. The solvents were evaporated under reduced pressure. The residue was washed by water and ethanol. The solid product of 2,5-thiophenediamide (**3**) was collected and dried. Yield: 0.84 g (60%).  $^1\text{H NMR } \delta$  (ppm in DMSO): 8.06 (s, 2H, amide,  $\text{NH}_2$ ), 7.68 (s, 2H, thiophene, CH), 7.54 (s, 2H, amide,  $\text{NH}_2$ ).

The product of **3** (0.68 g, 4 mmol) and lawesson reagent (1.62 g, 4 mmol) were mixed in 20 mL of toluene, giving a white suspension. With stirring, the reaction was heated at reflux for 6 h. After cooling down to room temperature, the yellow solid was collected by filtration and then, washed using a small amount of ethanol. Yield: 0.36 g (43%).  $^1\text{H NMR } \delta$  (ppm in DMSO): 9.81 (s, 2H, amide,  $\text{NH}_2$ ), 9.25 (s, 2H, amide,  $\text{NH}_2$ ) 7.62 (s, 2H, thiophene, CH).

**Preparation of 2,5-thienylenedithiocarboxylic acid (4).** 2,5-thiophenedicarboxylic chloride (**2**) (1.7 g, 8.2 mmol) and thioacetamide (2.4 g, 32 mmol) were mixed in 60 ml of benzene under nitrogen. The mixture was stirred in 35°C for 4 h, sodium hydroxide solution (8.2 mmol NaOH in 30 mL  $\text{H}_2\text{O}$ ) was added. After separation from the organic layer, to the aqueous phase was dropwise added dilute hydrochloric acid to produce yellow solid. Methylene chloride (20 mL) was added and the extract was dried with anhydrous  $\text{MgSO}_4$ . The solvents were evaporated under reduced pressure. The solid was collected and dried under vacuum. Yield: (1.2 g, 70%).  $^1\text{H NMR } \delta$  (ppm in  $\text{CDCl}_3$ ): 7.68 (s, 2H, thiophene, CH), 2.57 (s, 2H, SH).

**Preparation of 2,5-thiophenebis(dithiocarboxyl) (9).** To a solution of 2,5-thiophenedicarboxylic acid (**1**) (2.92 g, 17 mmol) in ethanol (80 mL) was added 2 mL of sulfuric acid (98%). The resultant solution was refluxed at 85 °C for 72 h. After removal of the solvent reduced pressure, water (30 mL) was added, and then, diethyl ether (3 × 30 mL) was used to extract the product. The combined extracts were dried using anhydrous  $\text{MgSO}_4$ . The solvent was evaporated and solid product collected. Yield: 3.2 g (82%). This material (**6**) was used for preparation of **7** without further purification.

In the ice water bath,  $\text{LiAlH}_4$  (0.50 g, 13.2 mmol) suspended in 30 mL of THF was transferred slowly to a solution of 2,5-thiophenediethylcarboxylate (**6**) (1.5 g, 6.6 mmol in 50 mL of THF). The mixture was stirred at low temperature for 30 min and then, at room temperature for additional 30 min. The reaction was heated at reflux for 24 h. After cooling down, the reaction was quenched by addition of water with great caution and then, 20 mL of NaOH solution (15%) was added. After removing the majority of THF by rotavapor, methylene chloride was added to extract the organic materials. The combined organic extracts were dried over  $\text{MgSO}_4$ . Evaporation of the solvent gave a light-yellow liquid. Yield: 0.5 g (52%). This material (**7**) was used for preparation of **8** without purification.

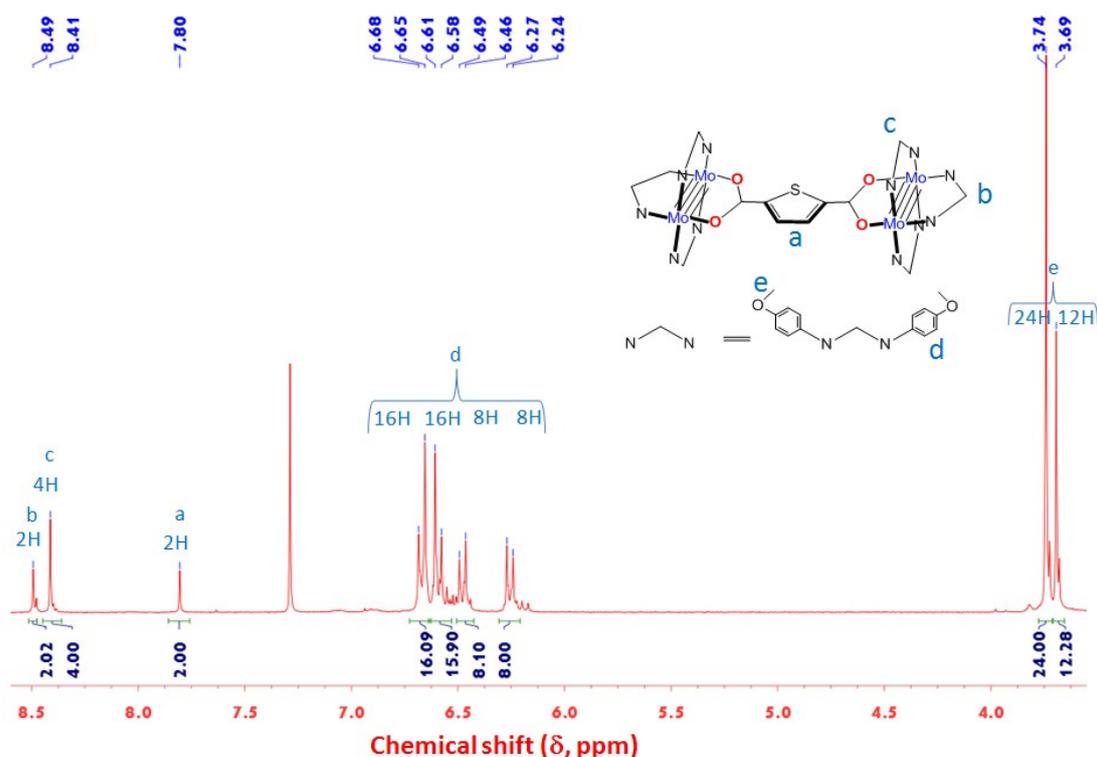
2,5-thiophenebis(hydroxymethyl) (**7**) (1 g, 7 mmol) was dissolved in anhydrous ether (40 ml) under a nitrogen atmosphere, to which 15 mL of HBr solution (48% in  $\text{H}_2\text{O}$ ) was added at 0°C. The solution was kept stirring at room temperature for 24 h, followed by addition of water (30 mL). The organic layer was separated. The aqueous layer was extracted twice with ether (2×25 mL). The combined extracts were dried over anhydrous  $\text{MgSO}_4$ . Removal of the solvent

afforded 2,5-thiophenbis(bromomethyl) (**8**) as a brown solid. Yield: (1.1, 58%). This material (**8**) was used for preparation of **9** without purification.

Sodium methoxide (1.21 g, 22.4 mmol) and elemental sulfur (0.72 g, 22.4 mmol) were mixed in anhydrous methanol (80 mL) in a 250-mL Schlenk flask. The mixture was heated to 70 °C and refluxed for 1 hour and then, **8** (1.5 g, 5.6 mmol) was added. The reaction was heated at reflux for additional 24 h. After that, it was cooled to room temperature first and then, to ~ 5°C in an ice bath. The solid materials were removed by filtration at low temperature. The filtrate was evaporated under reduced pressure. The red residue was dissolved in water (50 mL). The aqueous solution was washed using diethyl ether (3 × 20 mL). Then, dilute hydrochloric acid (1 M, 60 mL) was added; the water layer was extracted with methylene chloride (3 × 20 mL). The organic components were combined and dried over anhydrous MgSO<sub>4</sub>. Removal of the solvent gave a red solid product of **9**. Yield: (0.4 g, 30%). <sup>1</sup>H NMR δ (ppm in CDCl<sub>3</sub>): 6.86(s, 2H, CH), 1.25(s, 2H, SH).

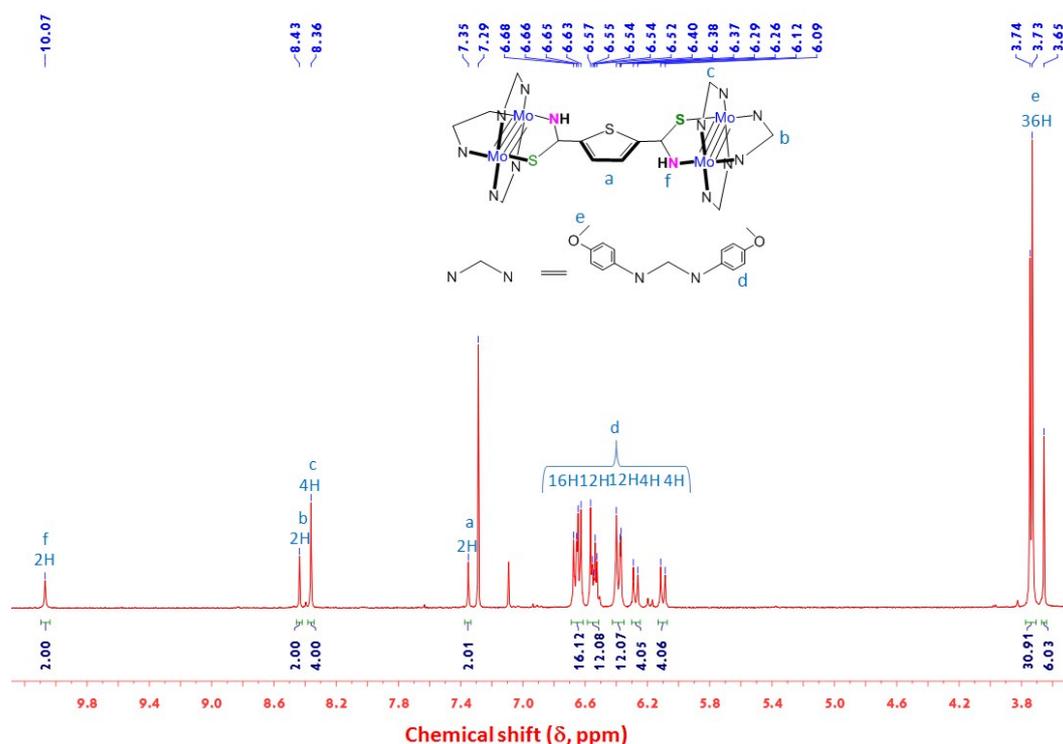
**General procedure for preparation of [OO–thi–OO], [NS–thi–NS], [OS–thi–OS] and [SS–thi–SS].** A solution of sodium ethoxide (0.0272 g, 0.4 mmol in 10 mL ethanol) was added to a THF solution (30 mL) having Mo<sub>2</sub>(DAniF)<sub>3</sub>(O<sub>2</sub>CCH<sub>3</sub>) (0.4064 g, 0.4 mmol) and 2,5-thiophenedicarboxylic acid (**1**) (0.0344 g, 0.2 mmol) for [OO–thi–OO] (or 2,5-thiophenedithioamide (**5**) (0.0405 g, 0.2 mmol) for [NS–thi–NS], 2,5-thiophenedithiocarboxylic acid (**4**) (0.0409 g, 0.2 mmol) for [OS–thi–OS] and 2,5-thiophenebis(dithiocarboxyl) (**9**) (0.0473 g, 0.2 mmol) for [SS–thi–SS]). The solution was stirred at room temperature for 5 h. The solvent was evaporated under reduced pressure. The residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) and the solution filtered through a Celite-packed funnel. The filtrate was evaporated under reduced pressure. The residue was washed with ethanol (3 × 15 mL) and then, the solid product was collected by filtration. The product was dried under vacuum. Yield for [OO–thi–OO] (dark red powder): 0.26 g, 63% yield; for [NS–thi–NS] (blue powder): 0.28 g, 66% yield; for [OS–thi–OS] (blue-green): 0.33 g, 78% yield; for [SS–thi–SS] (green powder): 0.3 g, 71% yield.

### <sup>1</sup>H NMR characterization.

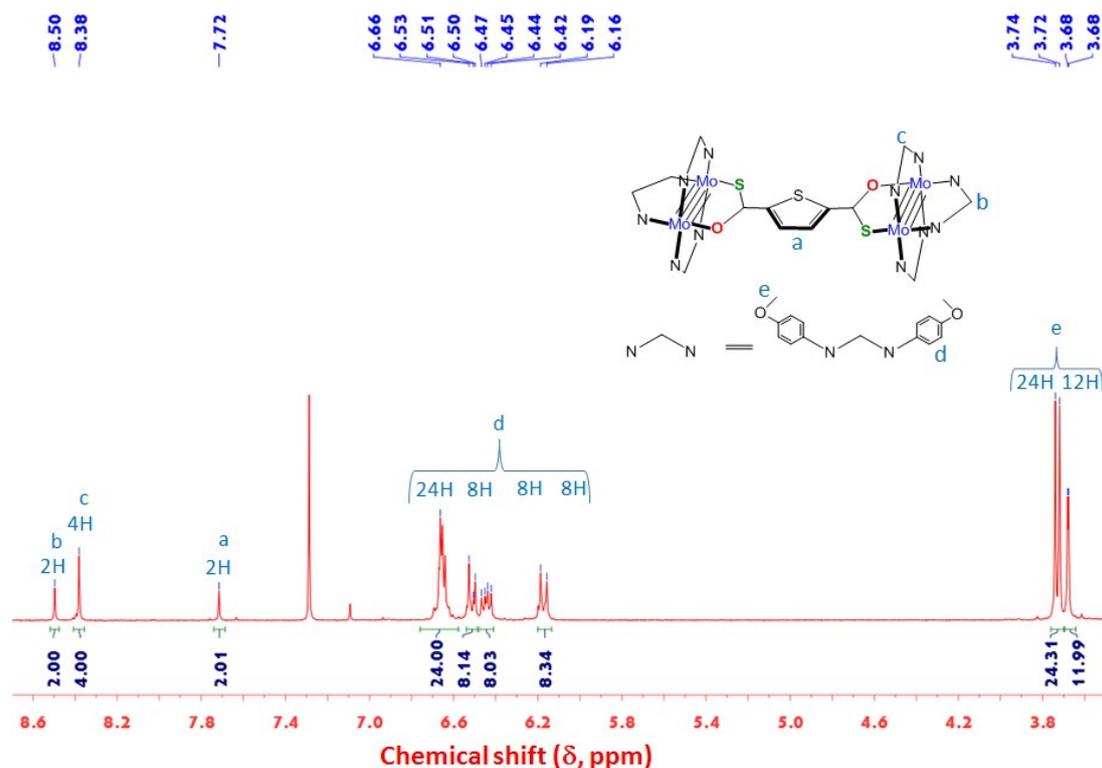


**Figure S8.** The <sup>1</sup>H NMR spectrum for [OO–thi–OO]. <sup>1</sup>H NMR δ (ppm in CDCl<sub>3</sub>): 8.49 (s, 2H, NCHN), 8.41 (s, 4H, NCHN), 7.80 (s, 2H, thiophene, CH), 6.65 (d, 16H, aromatic, CH), 6.58 (d, 16H, aromatic, CH), 6.46 (d, 8H, aromatic, CH),

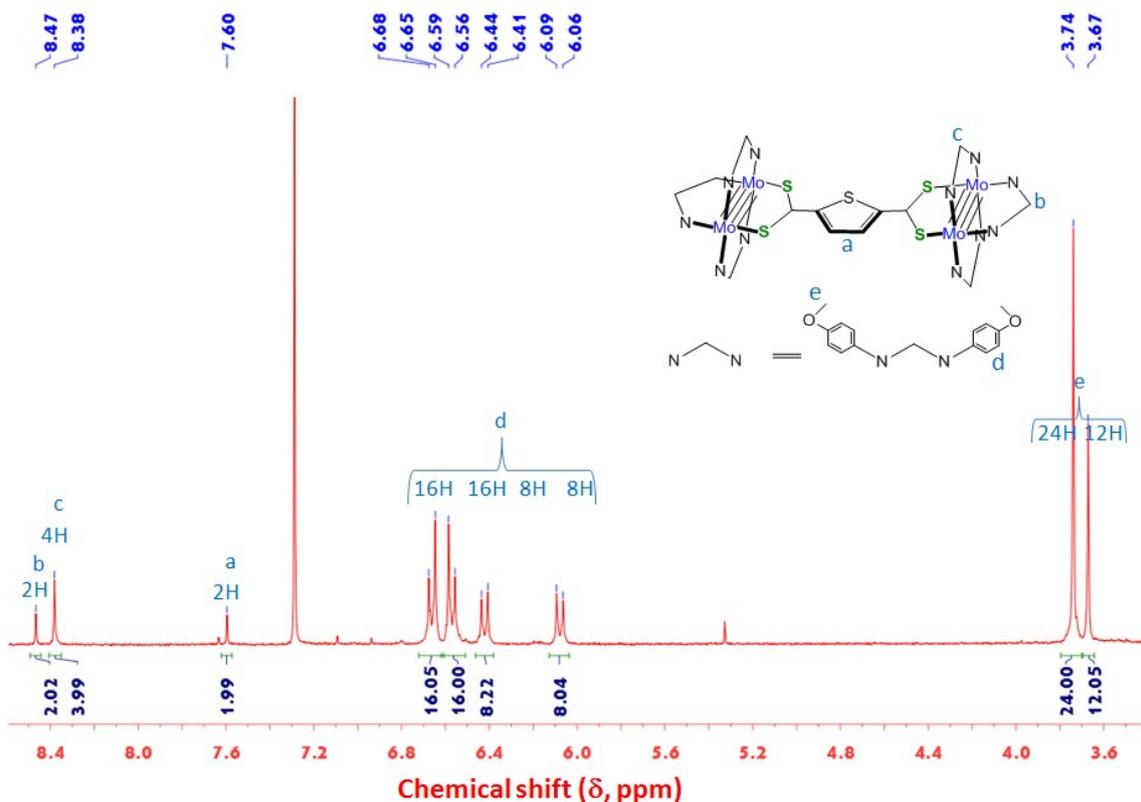
6.24 (d, 8H, aromatic, CH), 3.74 (s, 24H, OCH<sub>3</sub>), 3.69 (s, 12H, OCH<sub>3</sub>). UV-vis,  $\lambda_{\text{max}}$  nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 510 (14049). Anal. Calcd for C<sub>96</sub>H<sub>92</sub>Mo<sub>4</sub>N<sub>12</sub>O<sub>16</sub>S: C, 55.28; H, 4.44; N, 8.06; S, 1.54. Found: C, 55.20; H, 4.49; N, 8.11; S, 1.52.



**Figure S9.** The <sup>1</sup>H NMR spectrum for [NS-thi-NS]. <sup>1</sup>H NMR  $\delta$  (ppm in CDCl<sub>3</sub>): 10.07 (s, 2H, NH), 8.43 (s, 2H, NCHN), 8.36 (s, 4H, NCHN), 7.35 (s, 2H, thiophene, CH), 6.65 (t, 16H, aromatic, CH), 6.55 (t, 12H, aromatic, CH), 6.38 (d, 12H, aromatic, CH), 6.29 (d, 4H, aromatic, CH), 6.09 (d, 4H, aromatic, CH), 3.74 (s, 14H, OCH<sub>3</sub>), 3.73 (s, 16H, OCH<sub>3</sub>), 3.65 (s, 6H, OCH<sub>3</sub>). UV-vis,  $\lambda_{\text{max}}$  nm ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 610 (24326). Anal. Calcd for C<sub>96</sub>H<sub>94</sub>Mo<sub>4</sub>N<sub>14</sub>O<sub>12</sub>S<sub>3</sub>: C, 54.50; H, 4.48; N, 9.27; S, 4.55. Found: C, 54.41; H, 4.42; N, 9.38; S, 4.59.



**Figure S10.**  $^1\text{H}$  NMR spectrum for [OS–thi–OS].  $^1\text{H}$  NMR  $\delta$  (ppm in  $\text{CDCl}_3$ ): 8.50 (s, 2H, NCHN), 8.38 (s, 4H, NCHN), 7.72 (s, 2H, thiophene, CH), 6.64 (d, 24H, aromatic, CH), 6.47 (d, 8H, aromatic, CH), 6.44 (d, 8H, aromatic, CH), 6.16 (d, 8H, aromatic, CH), 3.74 (d, 12H,  $\text{OCH}_3$ ), 3.72 (s, 12H,  $\text{OCH}_3$ ), 3.68 (s, 6H,  $\text{OCH}_3$ ), 3.68 (s, 6H,  $\text{OCH}_3$ ). UV–vis,  $\lambda_{\text{max}}$  nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 691 (28167). Anal. Calcd for  $\text{C}_9\text{H}_9\text{Mo}_4\text{N}_{12}\text{O}_{14}\text{S}_3$ : C, 54.45; H, 4.38; N, 7.94; S, 4.54. Found: C, 54.57; H, 4.39; N, 7.85; S, 4.50.



**Figure S11.**  $^1\text{H}$  NMR spectrum for [SS–thi–SS].  $^1\text{H}$  NMR  $\delta$  (ppm in  $\text{CDCl}_3$ ): 8.47 (s, 2H, NCHN), 8.38 (s, 4H, NCHN), 7.60 (s, 2H, thiophene, CH), 6.65 (d, 16H, aromatic, CH), 6.56 (d, 16H, aromatic, CH), 6.41 (d, 8H, aromatic, CH), 6.06 (d, 8H, aromatic, CH), 3.74 (s, 24H,  $\text{OCH}_3$ ), 3.67 (s, 12H,  $\text{OCH}_3$ ). UV–vis,  $\lambda_{\text{max}}$  nm ( $\epsilon$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ): 826 (31024). Anal. Calcd for  $\text{C}_9\text{H}_9\text{Mo}_4\text{N}_{12}\text{O}_{12}\text{S}_5$ : C, 53.63; H, 4.31; N, 7.82; S, 7.46. Found: C, 53.75; H, 4.33; N, 7.77; S, 7.37.

## Notes and references

<sup>1</sup> C. Lin, J. D. Protasiewicz, E. T. Smith, T. Ren, *Inorg. Chem.* 1996, **35**, 6422–6428.

<sup>2</sup> F. A. Cotton, C. Y. Liu, C. A. Murillo, D. Villagr.n, X. Wang, *J. Am. Chem. Soc.* 2003, **125**, 13564–13575.