**Supporting Information**

**Manganese(I) Diimine(tricarbonyl) Complexes with a Redox-active Free Catechol Unit: Redox-induced Molecular Conversion of Catechol to Quinone by Electrochemical Redox Reactions on the Complex**

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**Table S1.** Crystallographic data for the ligands.

|  |  |  |
| --- | --- | --- |
| **Parameter** | **bpyCat** | **bpyOMe** |
| Formula | C16H12N2O2 | C18H16N2O2 |
| Formula weight | 264.28 | 292.34 |
| Temperature (K) | 153 | 293 |
| Crystal System | triclinic | orthorhombic |
| Space group | *P*-1 (#2) | *Iba*2 (#45) |
| *a* (Å) | 9.8588(9) | 18.9992(8) |
| *b* (Å) | 10.1442(9) | 25.0773(10) |
| *c* (Å) | 13.7612(13) | 6.1577(3) |
| *α* (Å) | 82.166(2) | 90 |
| *β* (Å) | 84.4945(19) | 90 |
| *γ* (Å) | 65.0593(17) | 90 |
| *V* (Å3) | 1235.1(2) | 2933.8(2) |
| *Z* | 4 | 8 |
| Calcd density (g/cm3) | 1.421 | 1.324 |
| *μ* (Mo *Kα*)(mm-1) | 9.57 | 8.75 |
| No. unique refins | 12867 | 14613 |
| No. obsd refins | 5585 | 3345 |
| Refinement method | Full-matrix least squares on *F*2 | |
| Parameters | 365 | 199 |
| *R* (*I* > 2*σ*(*I*)) 1 | 0.0579 | 0.0517 |
| *wR* (all data) 2 | 0.1414 | 0.1370 |
| *S* | 1.013 | 1.087 |

1*R* = Σ(||*F*o| − |*F*c||)/Σ|*F*o|; 2 *wR* = {Σ*w*(*F*o2 − *F*c2)2/Σ*w*(*F*o2)2}1/2.

**Table S2.** Crystallographic data for the Mn(I) complexes.

|  |  |  |
| --- | --- | --- |
| **Parameter** | **[MnBr(CO)3(bpyCat)] (1)** | **[MnBr(CO)3(bpyOMe)]** |
| Formula | C19H12BrMnN2O5 | C21H16BrMnN2O5 |
| Formula weight | 483.16 | 511.21 |
| Temperature (K) | 153 | 153 |
| Crystal System | monoclinic | triclinic |
| Space group | *P*21/*c* (#14) | *P*-1 (#2) |
| *a* (Å) | 17.0846(6) | 10.193(3) |
| *b* (Å) | 11.0741(4) | 10.196(3) |
| *c* (Å) | 9.3432(4) | 10.964(3) |
| *α* (Å) | 90 | 67.552(10) |
| *β* (Å) | 93.4362(10) | 79.869(11) |
| *γ* (Å) | 90 | 71.327(9) |
| *V* (Å3) | 1764.52(11) | 995.8(5) |
| *Z* | 4 | 2 |
| Calcd density (g/cm3) | 1.819 | 1.705 |
| *μ* (Mo *Kα*)(mm-1) | 305.50 | 271.18 |
| No. unique refins | 10217 | 18079 |
| No. obsd refins | 4490 | 4025 |
| Refinement method | Full-matrix least squares on *F*2 | |
| Parameters | 271 | 253 |
| *R* (*I* > 2*σ*(*I*)) 1 | 0.0478 | 0.0421 |
| *wR* (all data) 2 | 0.1316 | 0.1236 |
| *S* | 1.062 | 1.074 |

1*R* = Σ(||*F*o| − |*F*c||)/Σ|*F*o|; 2 *wR* = {Σ*w*(*F*o2 − *F*c2)2/Σ*w*(*F*o2)2}1/2.

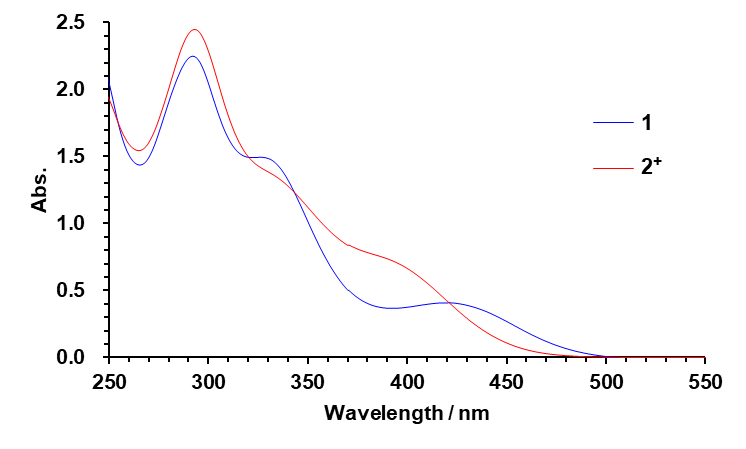
**Table S3.** Orbital contribution data for **1** and **2**+ in CH3CN.

**1**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| MOs | *E* / eV | Contribution / % | | | | |
| Mn | Br | bpyCat | | COs |
| bpy | Cat |
| LUMO | –2.32 |  |  | 87 | 5 |  |
| HOMO | –5.88 |  |  | 9 | 84 |  |
| HOMO–1 | –6.20 | 41 | 45 |  |  | 6 |
| HOMO–2 | –6.24 | 36 | 49 |  |  |  |

**2**+

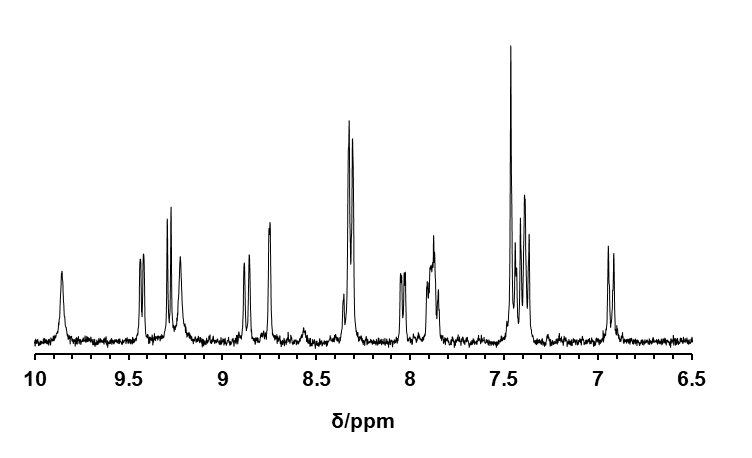
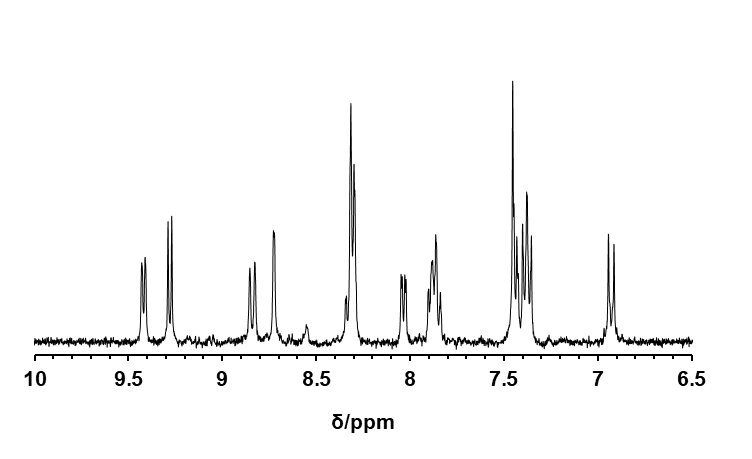
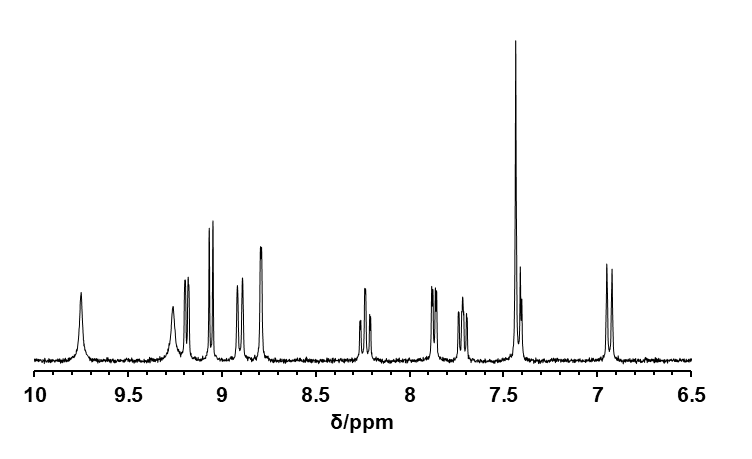
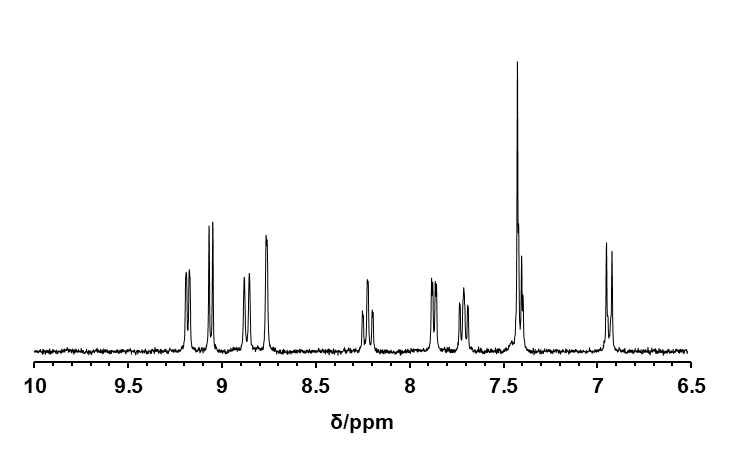
|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| MOs | *E* / eV | Contribution / % | | | | |
| Mn | py | bpyCat | | COs |
| bpy | Cat |
| LUMO | –2.53 |  |  | 89 | 5 |  |
| HOMO | –5.98 |  |  | 9 | 89 |  |
| HOMO–1 | –6.76 | 38 |  | 7 | 45 |  |
| HOMO–2 | –6.83 | 70 |  | 8 |  | 17 |

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**Fig. S1.** Absorption spectra of **1** and **2**+ in CH3CN (*c* = 1.0×10-4 mol dm-3).

**2**+

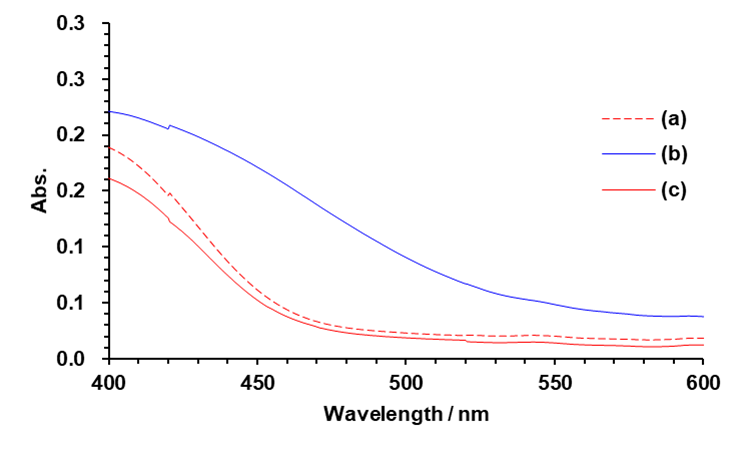
**1**



**2**+ + D2O

**1** + D2O

**Fig. S2.** 1H NMR spectra of **1** and **2**+ in DMSO-*d*6. The circle sign (•) denotes the OH proton signals.



**at 0.9 V**

**at -0.6 V**

**Fig. S3.** Absorption spectral changes during controlled-potential electrolysis in CH3CN of (a) **2**+; (b) after electrolysis of **2**+ at 0.9 V; (c) subsequent re-electrolysis of (b) at –0.6 V. These spectra correspond to **Fig. 6a**, **b**, and **c**, respectively.