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# The role of nano-sized manganese oxides in the oxygen-evolution reaction by manganese complexes: Towards a complete picture

**Mohammad Mahdi Najafpour,*[a,b] Małgorzata Hołyńska,[c] Amir Nasser Shamkhali,[d] Sayed Habib Kazemi,[a,b] Warwick Hillier,[e] Emad Amini,[a] Mostafa Ghaem Maghami,[a] Davood Jafarian Sedigh, ‡[a] Atefeh Nemati Moghaddam, ‡[a] Rahim Mohamadi, ‡[a] Sasan Zaynalpoor‡[a] and Katrin Beckmann‡[e]**

*a Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan 45137-66731, Iran*

*b Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Iran.*

*cFachbereich Chemie and Wissenschaftliches Zentrum für Materialwissenschaften (WZMW), Philipps-Universität Marburg, Hans-Meerwein-Straße, D-35032 Marburg, Germany*

*d Department of Applied Chemistry, Faculty of Sciences, University of Mohaghegh Ardabili, Ardabil, P. O. Box: 56199-11367, Iran.*

*e Research School of Biology, Canberra, ACT 0200, Australia*

**Corresponding author. E-mail address: mmnajafpour@iasbs.ac.ir (M.M. Najafpour);Tel.: +98 241 4153201; Fax.: +98 241 4153232*;

*‡These authors contributed equally to the work.*

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## Experiment

## Synthesis

**Complex 1** ($Mn(2\text{-pic})_3 \cdot H_2O$), 2-pic: 2-pyridinecarboxylate):[1] The complex was prepared with a new synthetic route by the reaction of 2-pyridinecarboxylic acid (6.0 mmol, 739 mg) and $Mn(OAc)_2 \cdot 4H_2O$ (2.0 mmol, 490 mg) in ethanol (20 mL). The mixture was stirred for about 4 h at room temperature. Slow addition of an aqueous solution (4 mL) of $(NH_4)_2Ce(NO_3)_6$ (2.0 mmol, 1.096 g) to the solution resulted in a red solution, which was filtered and kept at room temperature. Red crystalline material deposited in 2 days, was filtered off, and washed with cold water (1 ml). Anal. Calcd for complex (**1**) (%): C, 49.2; H, 3.2; N, 9.6; Found: C, 49.1; H, 3.3; N, 9.8.

**Complex 2** ($Mn(2\text{-pic})_2 \cdot 2H_2O$), 2-pic: 2-pyridinecarboxylate):[2] The complex was prepared by dissolving guanidinium carbonate (3.2 mmol, 576 mg) and 2-pyridinecarboxylic acid (6.0 mmol, 739 mg) in water (20 ml). The mixture was stirred for about 1 h at 50° C. Then Mn(II) chloride (2.0 mmol, 252 mg) was added to this solution and stirred for about 3 h at room temperature. This solution yielded yellow crystals of the complex after 10 d. The yellow crystals were filtered off, washed with 5 mL of cool water, 5 mL EtOH and then dried in air. Anal. Calcd for complex (**2**) (%): C, 43.0; H, 3.6; N, 8.4; Found: C, 42.8; H, 3.7; N, 8.4.

**Complex 3** ($Mn(phen)_3(PF_6)_2$):[3] The complex was prepared by the reaction of $Mn(CH_3CO_2)_2 \cdot 4H_2O$ (2.0 mmol, 490 mg), 1,10-phenanthroline (3.0 mmol, 0.54 g) and $NaPF_6$ (10.0 mmol, 1.68 g) in MeOH (30 ml). This solution yielded yellow crystals of the complex **3** after 24 h. The yellow crystals were filtered off, washed with 5 mL of cool water, 5 mL EtOH and then dried in air. Anal. Calcd for complex (**3**) (%): C, 48.8; H, 2.7; N, 9.5; Found: C, 48.1; H, 2.2; N, 9.2.

**Complex 4** ($Mn(phen)_2(NO_3)_2 \cdot 2H_2O$):[4] The complex was prepared by the reaction of $Mn(NO_3)_2 \cdot 2H_2O$ (2.0 mmol, 430 mg) and 1,10-phenanthroline (4.0 mmol, 720 mg) in 20 ml EtOH/water (1/1). This solution yielded yellow crystals of the complex **4** after 4 h. The yellow crystals were filtered off, washed with 5 mL of cool water, 5 mL EtOH and then dried in air. Anal. Calcd for complex (**4**) (%): C, 50.1; H, 3.5; N, 14.6; Found: C, 49.3; H, 3.2; N, 14.1.

**Complex 5** ($Mn(phen)(H_2O)_4SO_4 \cdot 2H_2O$):[5] The complex was prepared by the reaction of $MnSO_4$ (2.0 mmol, 300 mg) and 1,10-phenanthroline (2.0 mmol, 360 mg) in 20 ml water. The mixture was refluxed for 24 h. This solution yielded yellow crystals of the complex **5** after 45 h. The yellow crystals were filtered off, washed with 5 mL of cool water, 5 mL EtOH and then dried in air. Anal. Calcd for complex (**5**) (%): C, 32.8; H, 4.6; N, 6.4; Found: C, 32.2; H, 4.2; N, 6.3.

**Complex 6** ($Mn(bpy)_3(NO_3)_2 \cdot 3H_2O$): The complex was prepared by combining $Mn(NO_3)_2 \cdot 2H_2O$ (2 mmol, 430 mg) and 1,10-bipyridine (6.0 mmol, 940 mg) in 20 ml EtOH/water (1/1). The mixture was refluxed for 3 h. This solution yielded yellow crystals of the complex **6** after 1 week. The yellow crystals were filtered off, washed with 5 mL of cool water, 5 mL EtOH and then dried in air. Anal. Calcd for complex (**6**) (%): C, 51.4; H, 4.3; N, 16.0; Found: C, 50.9; H, 4.2; N, 15.9.

**Complex 7** ($Mn(bpy)_2(NO_3)_2 \cdot 2H_2O$): The complex was prepared by the reaction of $Mn(NO_3)_2 \cdot 2H_2O$ (2.0 mmol, 430 mg) and 1,10-bipyridine (4.0 mmol, 620 mg) in 20 ml EtOH/water (1/1). The mixture was refluxed for 3 h. This solution yielded yellow crystals of the complex **7** after 1 week. The yellow crystals were filtered off, washed with 5 mL of cool water, 5 mL EtOH and then dried in air. Anal. Calcd for complex (**7**) (%): C, 45.5; H, 3.8; N, 15.9; Found: C, 45.4; H, 3.2; N, 15.3.

**Complex 8** ($Mn(bpy)(NO_3)_2 \cdot 4H_2O$): The complex was prepared by the reaction of $Mn(NO_3)_2 \cdot 2H_2O$ (2.0 mmol, 430 mg) and 1,10-bipyridine (2.0 mmol, 310 mg) in 20 ml EtOH/water (1/1). The mixture was refluxed for 3 h. This solution yielded yellow crystals of the complex **8** after one week. The yellow crystals were filtered off, washed with 5 mL of cool water, 5 mL EtOH and then dried in air. Anal. Calcd for complex (**8**) (%): C, 29.5; H, 3.9; N, 13.8; Found: C, 30.5; H, 3.2; N, 13.3.

**Complex 9** ($Mn(dipic)_2(Gua)_2$: Gua: Guanidinium, dipic: Pyridine-2,6-dicarboxylate):[6] The complex was prepared by dissolving guanidinium carbonate (4.0 mmol, 720 mg) and pyridine-2,6-dicarboxylic acid (2.0 mmol, 334mg) in water (20 ml). The mixture was stirred for about 1 h at room temperature. Then Mn(II) chloride (1.0 mmol, 126 mg) was

added to this solution and stirred for about 3 h at room temperature. This solution yielded yellow crystals of the complex **9** after 10 d. The yellow crystals were filtered off, washed with 5 mL of cool water, 5 mL EtOH and then dried in air. Anal. Calcd for complex (**9**) (%): C, 35.5; H, 4.1; N, 20.7; Found: C, 35.8; H, 4.9; N, 20.3.

**Complex 10** ($Mn(Pzdc)(H_2O)_4$: $PzdcH_2$: 2,3-Pyrazinedicarboxylic acid)**:**[7] A 10 ml amount of an aqueous solution of $MnCl_2{\cdot}4H_2O$ (1.0 mmol, 198 mg) add to 10 ml of an aqueous solution of $PzdcH_2$ (1.0 mmol, 168 mg) and stirred for about 3 h at room temperature. The pale yellow prism crystals formed after 2 d. Pale yellow crystals were filtered off, washed with 5 mL of cooled water, 5 mL EtOH and then dried in air.

**Complex 11** ($Mn(Gly)_2{\cdot}4H_2O$: Gly: Glycine$\cdot 4H_2O$):[8] $LiOH{\cdot}H_2O$ (5.50 mmol, 231 mg) was dissolved in ethanol (70 mL) and glycine (5.90 mmol, 443 mg) was added to the solution. The mixture was refluxed for 2 h. To the solution was added $Mn(NO_3)_2{\cdot}2H_2O$ (2.7 mmol, 580 mg) and refluxing was continued for further 1.5 h. The resulting suspension was cooled down to room temperature and the solid product was filtered off, washed with ethanol and air-dried. Anal. Calcd for complex (**11**) (%): C, 17.5; H, 5.9; N, 10.2; Found: C, 17.4; H, 5.2; N, 10.3.

**Complex 12 (**$Mn(Asp)_2{\cdot}4H_2O$, Asp: Aspartate):[8] To a solution of $Ba(OH)_2{\cdot}8H_2O$ (8.0 mmol, 2.85 g) in water (90 mL) was added aspartic acid (16.0 mmol, 2.13 g) and the solution was stirred at room temperature for 2 h. The resulting solution was filtered and the supernatant was evaporated to ~20 mL. To the supernatant ethanol (10 mL) was added to give a white suspension of the barium salt of the respective amino acid and this was concentrated to dry residue. The solid was washed with ethanol and air-dried. To a solution of the amino acid barium salt in water (60 mL) was added a solution of $MnSO_4{\cdot}H_2O$ (8 mmol, 1.35 g) in water (20 mL) and the resulting suspension was stirred, at room temperature, for 2 h. The solid was filtered off and the supernatant was evaporated to 25 mL. To the supernatant was added ethanol (10 mL) to give a suspension, which was concentrated to yield a solid residue. The solid was washed with ethanol and air-dried for several days. Anal. Calcd for complex (**12**) (%): C, 24.6; H, 5.2; N, 7.2; Found: C, 24.7; H, 5.5; N, 7.3.

**Complex 13** $Mn(Pzdc)(H_2O)_2{\cdot}2H_2O$, $PzdcH_2$: 2,3-Pyrazinedicarboxylic acid:[7] 2,3-Pyrazinedicarboxylic acid (1 mmol, 0.17 g) and NaOH (2 mmol, 0.08 g) were dissolved in water and methanol mixture (20 ml, *v/v* 1:1). To this solution, $Mn(CH_3COO)_2{\cdot}4H_2O$ (1 mmol, 0.25 g) was added and the resulting mixture was stirred and refluxed at 343 K for 5 h, then cooled to room temperature. After filtration and evaporation in air for a week, pink block-shaped crystals were obtained.

**Complex 14** ($Mn(Imd)(H_2O)_2$), Imd: Imidazole-4,5-di-carboxylate):[9] To a suspension of $MnCl_2{\cdot}4H_2O$ (0.40 g, 2 mmol) and the ligand (0.31 g, 2 mmol) in water (50 ml), NaOH (0.1 M) was added dropwise, under continuous stirring until the mixture became clear. The mixture was heated at 120 ºC for 10 h under hydrothermal conditions. After filtration and evaporation in air for a week, pale-yellow crystals of **14** were formed. Anal. Calcd for complex (**14**) (%): C, 29.9; H, 2.5; N, 14.0; Found: C, 29.5; H, 2.6; N, 14.1.

**Complex 16** ($Mn(tptz)Cl_2(H_2O)$), tptz: 2,4,6-tris(2-pyridyl)-1,3,5-triazine):[10] The complex was prepared by dissolving Mn(II) chloride (1 mmol, 126 mg) and tptz (1 mmol, 312 mg) in water (30 ml); the mixture was stirred for about 1 h at room temperature under nitrogen atmosphere. The solution was then evaporated on a steam bath to 10 mL and cooled down to room temperature. Orange crystals of complex **16** separated and were filtered off, washed with 5 mL of cool water and then dried in air. IR ($cm^{-1}$): 3445 (b), 3360 (s), 1526 (s), 1480 (m), 1379 (s), 1045 (w), 809 (s).

## Tables

Table S1. Selected X-ray data for **15, 17** and **18**.

| | **15** | **17** | **18** |
|---|---|---|---|
| Formula | $C_{24}H_{20}MnN_4O_4 \cdot 2(H_2O)$ | $C_{36}H_{24}MnN_4O_5 \cdot 4(H_2O)$ | $(C_5H_{10}MnN_2O_8) \cdot 1.5(H_2O)$ |
| Formula weight | 519.41 | 719.60 | 308.11 |
| Temperature [K] | 100(2) | 100(2) | 100(2) |
| λ [Å] | 0.71073 | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic | Orthorhombic |
| Space group | $P2_1/c$ | $P\bar{1}$ | Pbcn |
| a [Å] | 16.852 (3) | 12.731 (3) | 20.318 (4) |
| b [Å] | 9.292 (2) | 12.876 (3) | 11.781 (3) |
| c [Å] | 15.791 (3) | 22.096 (4) | 9.576 (2) |
| α [°] | | 93.88 (3) | |
| β [°] | 114.57 (3) | 100.00 (3) | |
| γ [°] | | 107.99 (3) | |
| V [$Å^3$] | 2248.8 (8) | 3364.1 (13) | 2292.2 (9) |
| Z, $\rho_{calc}$ [g $cm^{-3}$] | 4, 1.534 | 4, 1.421 | 8, 1.786 |
| μ [$mm^{-1}$] | 0.64 | 0.46 | 1.20 |
| F(000) | 1076 | 1492 | 1264 |
| Crystal size [mm] | 0.3 × 0.15 × 0.08 | 0.2 × 0.2 × 0.09 | 0.33 × 0.08 × 0.08 |
| θ range[°] | 1.33-25.00 | 1.68-25.00 | 2.00-26.75 |
| rflns: total/unique | 25571/3950 | 48816/11853 | 2435/0/159 |
| R(int) | 0.065 | 0.077 | 0.088 |
| Abs. corr. | numerical | numerical | numerical |
| Min., max. transmission factors | 0.846, 0.963 | 0.922, 0.969 | 0.762, 0.929 |
| Data/restraints/params | 3950/0/317 | 11853/0/901 | 2435/0/159 |
| GOF on $F^2$ | 0.81 | 0.84 | 0.96 |
| R1 [I > 2σ(I)] | 0.027 | 0.032 | 0.027 |
| $wR_2$ (all data) | 0.040 | 0.040 | 0.040 |
| Max., min. $\Delta\rho_{elect}$ [e $Å^{-3}$] | 0.28, -0.30 | 0.24, -0.37 | 0.39, -0.27 |

Table S2. Selected geometric parameters [Å, °] for **15, 17** and **18.**

| | | | |
|---|---|---|---|
| **1** | | | |
| Mn1—O1 | 2.2467 (16) | Mn1—N4 | 2.333 (2) |
| Mn1—N3 | 2.3170 (19) | Mn1—O4 | 2.3347 (15) |
| Mn1—N2 | 2.3187 (19) | Mn1—O3 | 2.3433 (16) |
| Mn1—N1 | 2.330 (2) | | |
| O1—Mn1—N3 | 84.30 (6) | N3—Mn1—O4 | 128.63 (6) |
| O1—Mn1—N2 | 83.48 (6) | N2—Mn1—O4 | 128.11 (6) |
| N3—Mn1—N2 | 69.35 (7) | N1—Mn1—O4 | 80.19 (6) |
| O1—Mn1—N1 | 89.55 (6) | N4—Mn1—O4 | 81.27 (6) |
| N3—Mn1—N1 | 138.62 (7) | O1—Mn1—O3 | 165.52 (6) |
| N2—Mn1—N1 | 69.30 (7) | N3—Mn1—O3 | 83.64 (6) |
| O1—Mn1—N4 | 90.38 (7) | N2—Mn1—O3 | 84.79 (6) |
| N3—Mn1—N4 | 69.31 (7) | N1—Mn1—O3 | 94.23 (6) |
| N2—Mn1—N4 | 138.61 (7) | N4—Mn1—O3 | 92.82 (6) |
| N1—Mn1—N4 | 151.82 (6) | O4—Mn1—O3 | 56.06 (5) |
| O1—Mn1—O4 | 138.41 (6) | | |
| **2** | | | |
| Mn1—O1W | 2.133 (2) | Mn2—N222 | 2.303 (2) |
| Mn1—O11 | 2.0944 (18) | Mn2—N212 | 2.312 (2) |
| Mn1—N221 | 2.263 (2) | O11—C11 | 1.282 (3) |
| Mn1—N211 | 2.276 (3) | O21—C11 | 1.242 (3) |
| Mn1—N111 | 2.302 (2) | O31—C111 | 1.269 (3) |
| Mn1—N121 | 2.317 (2) | O41—C111 | 1.259 (3) |
| Mn2—O2W | 2.130 (2) | O12—C14 | 1.270 (3) |
| Mn2—O12 | 2.1077 (18) | O22—C14 | 1.247 (3) |
| Mn2—N112 | 2.281 (2) | O32—C114 | 1.267 (3) |
| Mn2—N122 | 2.290 (3) | O42—C114 | 1.261 (3) |
| O11—Mn1—O1W | 92.37 (7) | O12—Mn2—O2W | 90.94 (8) |
| O11—Mn1—N221 | 98.70 (8) | O12—Mn2—N112 | 100.26 (8) |
| O1W—Mn1—N221 | 103.26 (8) | O2W—Mn2—N112 | 104.33 (8) |
| O11—Mn1—N211 | 97.51 (8) | O12—Mn2—N122 | 96.82 (8) |
| O1W—Mn1—N211 | 92.32 (8) | O2W—Mn2—N122 | 90.52 (8) |
| N221—Mn1—N211 | 156.94 (7) | N112—Mn2—N122 | 157.06 (7) |
| O11—Mn1—N111 | 89.79 (8) | O12—Mn2—N222 | 90.53 (8) |
| O1W—Mn1—N111 | 165.36 (9) | O2W—Mn2—N222 | 163.22 (9) |
| N221—Mn1—N111 | 90.71 (9) | N112—Mn2—N222 | 91.85 (9) |
| N211—Mn1—N111 | 73.03 (9) | N122—Mn2—N222 | 72.71 (9) |
| O11—Mn1—N121 | 169.25 (8) | O12—Mn2—N212 | 171.06 (8) |
| O1W—Mn1—N121 | 95.85 (8) | O2W—Mn2—N212 | 95.75 (8) |
| N221—Mn1—N121 | 72.69 (8) | N112—Mn2—N212 | 72.37 (8) |
| N211—Mn1—N121 | 89.09 (8) | N122—Mn2—N212 | 89.05 (8) |
| N111—Mn1—N121 | 84.00 (8) | N222—Mn2—N212 | 84.78 (8) |
| **3** | | | |
| Mn1—O1W | 2.1189 (13) | Mn1—O2W | 2.2119 (14) |
| Mn1—O3W | 2.1437 (15) | Mn1—O1 | 2.2169 (15) |
| Mn1—O4W | 2.1719 (15) | Mn1—N1 | 2.2650 (16) |
| O1W—Mn1—O3W | 86.48 (6) | O4W—Mn1—O1 | 168.79 (6) |
| O1W—Mn1—O4W | 95.37 (6) | O2W—Mn1—O1 | 88.03 (5) |
| O3W—Mn1—O4W | 88.94 (6) | O1W—Mn1—N1 | 165.21 (5) |
| O1W—Mn1—O2W | 83.63 (6) | O3W—Mn1—N1 | 103.82 (6) |
| O3W—Mn1—O2W | 170.04 (6) | O4W—Mn1—N1 | 95.41 (6) |
| O4W—Mn1—O2W | 93.23 (6) | O2W—Mn1—N1 | 85.67 (6) |

| | | | |
|---|---|---|---|
| O1W—Mn1—O1 | 95.84 (6) | O1—Mn1—N1 | 73.56 (6) |
| O3W—Mn1—O1 | 91.74 (6) | | |

Table S3. Hydrogen bonding parameters [Å, °] for **15, 17** and **18**.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| **1** | | | | |
| O1W—H1W1···O1 | 0.82 | 2.17 | 2.965 (2) | 165 |
| O1W—H1W2···O2W$^{i}$ | 0.82 | 2.06 | 2.873 (2) | 170 |
| O2W—H2W1···O2 | 0.82 | 2.02 | 2.837 (2) | 172 |
| O2W—H2W2···O3$^{ii}$ | 0.82 | 2.10 | 2.916 (2) | 173 |
| Symmetry codes: (i) *x*, *y*+1, *z*; (ii) *x*, -*y*+1/2, *z*+1/2. | | | | |
| **2** | | | | |
| O1W—H1W1···O31 | 0.82 | 1.93 | 2.729 (2) | 167 |
| O1W—H1W2···O41$^{i}$ | 0.82 | 1.81 | 2.626 (3) | 174 |
| O2W—H2W1···O32 | 0.82 | 1.93 | 2.744 (2) | 170 |
| O2W—H2W2···O42$^{ii}$ | 0.82 | 1.81 | 2.622 (3) | 172 |
| O3W—H3W1···O32 | 0.82 | 2.03 | 2.850 (3) | 175 |
| O3W—H3W2···O2W$^{ii}$ | 0.82 | 2.31 | 2.948 (3) | 135 |
| O4W—H4W1···O31$^{iii}$ | 0.82 | 2.02 | 2.833 (3) | 176 |
| O4W—H4W2···O1W$^{iv}$ | 0.82 | 2.27 | 2.938 (3) | 139 |
| O5W—H5W1···O3W | 0.82 | 1.97 | 2.790 (3) | 176 |
| O5W—H5W2···O7W$^{v}$ | 0.82 | 2.01 | 2.825 (2) | 175 |
| O6W—H6W1···O4W$^{vi}$ | 0.82 | 2.01 | 2.824 (3) | 169 |
| O6W—H6W2···O9W$^{vii}$ | 0.82 | 2.01 | 2.827 (3) | 178 |
| O7W—H7W1···O42$^{viii}$ | 0.82 | 1.98 | 2.797 (3) | 178 |
| O7W—H7W2···O10W$^{viii}$ | 0.82 | 1.96 | 2.771 (3) | 169 |
| O8W—H8W1···O41$^{ix}$ | 0.82 | 1.97 | 2.794 (3) | 177 |
| O8W—H8W2···O9W$^{iv}$ | 0.82 | 2.11 | 2.912 (2) | 166 |
| Symmetry codes: (i) -*x*, -*y*+2, -*z*; (ii) -*x*+2, -*y*+1, -*z*+1; (iii) -*x*+1, -*y*+2, -*z*; (iv) *x*+1, *y*, *z*; (v) -*x*+1, -*y*+1, -*z*+1; (vi) -*x*+1, -*y*+2, -*z*+1; (vii) -*x*, -*y*+1, -*z*+1; (viii) *x*-1, *y*, *z*; (ix) *x*+1, *y*-1, *z*; (x) *x*, *y*-1, *z*. | | | | |
| **3** | | | | |
| O1W—H1W1···O5W | 0.82 | 1.97 | 2.788 (2) | 177 |
| O1W—H1W2···O2$^{i}$ | 0.82 | 1.89 | 2.702 (2) | 175 |
| O2W—H2W1···O2$^{ii}$ | 0.85 | 1.88 | 2.719 (2) | 171 |
| O2W—H2W2···O1$^{i}$ | 0.85 | 1.90 | 2.752 (2) | 179 |
| O3W—H3W1···O6W | 0.82 | 1.97 | 2.783 (2) | 175 |
| O3W—H3W2···O4$^{iii}$ | 0.85 | 1.98 | 2.795 (2) | 163 |
| O4W—H4W1···O3$^{iv}$ | 0.82 | 1.94 | 2.753 (2) | 177 |
| O4W—H4W2···O5W$^{v}$ | 0.82 | 2.04 | 2.852 (2) | 174 |
| O5W—H5W1···O4$^{vi}$ | 0.82 | 1.92 | 2.7236 (19) | 169 |
| O5W—H5W2···O1$^{vii}$ | 0.82 | 2.39 | 3.0835 (19) | 143 |
| O5W—H5W2···O1$^{vii}$ | 0.82 | 2.39 | 3.0835 (19) | 143 |
| O5W—H5W2···O2W$^{vii}$ | 0.82 | 2.58 | 3.192 (2) | 133 |
| O6W—H6W1···O4$^{vi}$ | 0.82 | 2.04 | 2.836 (2) | 166 |
| N2—H2N···O3$^{iv}$ | 0.86 | 1.91 | 2.752 (2) | 167 |
| Symmetry codes: (i) -*x*+3/2, -*y*+3/2, *z*-1/2; (ii) *x*, -*y*+2, *z*-1/2; (iii) *x*, -*y*+2, *z*+1/2; (iv) -*x*+1, -*y*+2, -*z*; (v) *x*, -*y*+1, *z*-1/2; (vi) *x*, *y*-1, *z*; (vii) -*x*+3/2, *y*-1/2, *z*. | | | | |

Table S4 Selected optimized parameters of the complex 17 and its oxidized state (Å, °). Atom labeling scheme is in accordance with Figure 3 (see Article).

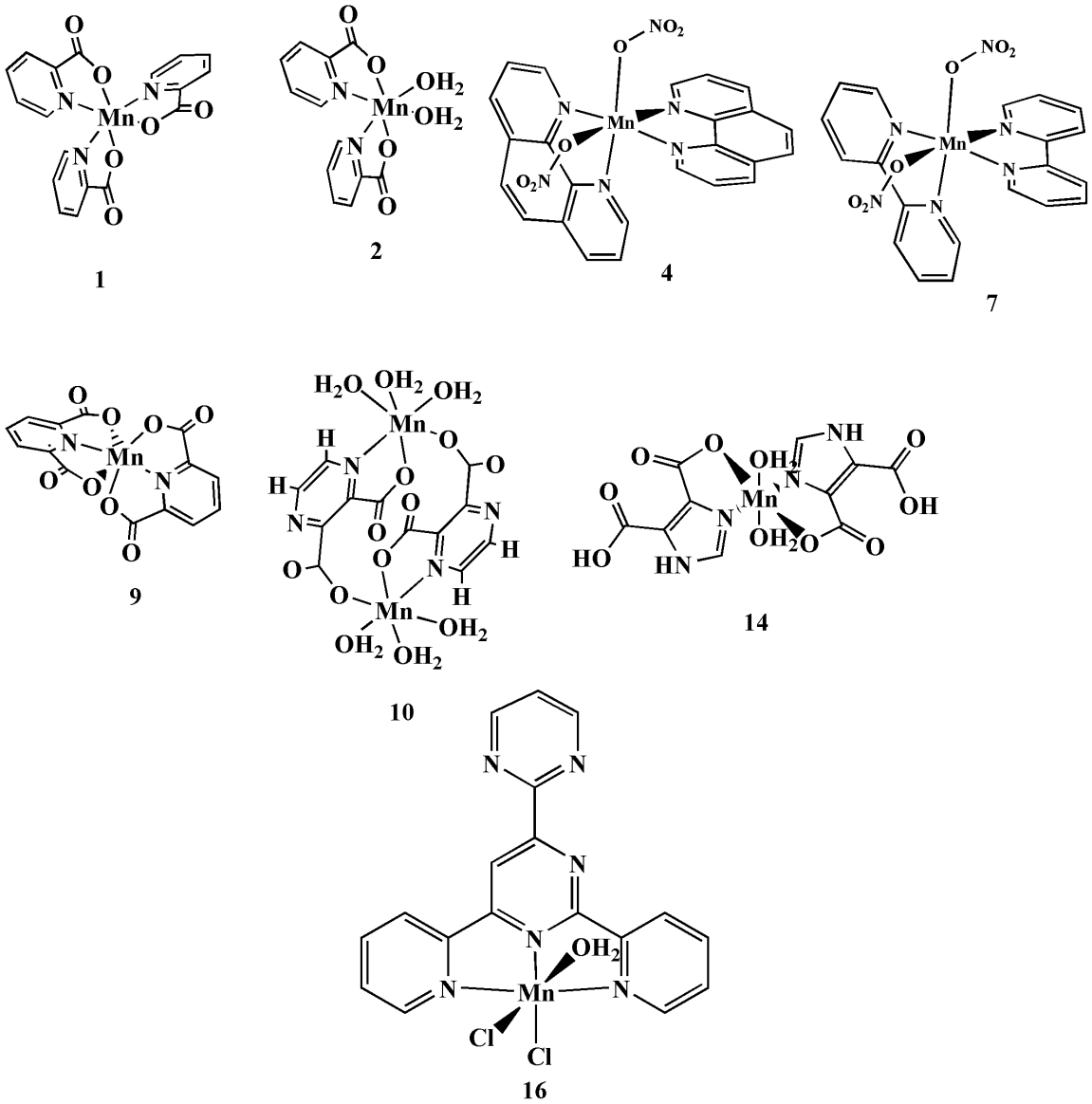
| parameter | Mn(II) | Mn(III) | parameter | Mn(II) | Mn(III) |
|---|---|---|---|---|---|
| Mn1-O1W | 2.0743 | 1.8503 | O1W-Mn1-O11 | 99.90 | 95.09 |
| Mn1-O11 | 2.1133 | 1.9742 | O1W-Mn1-N111 | 160.25 | 166.55 |
| Mn1-N111 | 2.3521 | 2.0630 | O1W-Mn1-N211 | 88.58 | 88.16 |
| Mn1-N211 | 2.2710 | 2.2002 | O11-Mn1-N111 | 91.64 | 89.20 |
| Mn1-N121 | 2.2990 | 2.2871 | O11-Mn1-N211 | 106.90 | 113.35 |
| Mn1-N221 | 2.4066 | 2.2399 | O1W-Mn1-N121 | 99.26 | 94.17 |
| O1W-H1W1 | 1.2587 | 1.7362 | O1W-Mn1-N221 | 90.80 | 92.20 |
| O1W-H1W2 | 0.9723 | 0.9794 | O11-Mn1-N121 | 83.85 | 82.36 |
| C111-O31 | 1.3341 | 1.3737 | O11-Mn1-N221 | 153.90 | 155.45 |
| C111-O41 | 1.2630 | 1.2471 | N111-Mn1-N211 | 72.66 | 78.44 |
| C11-O11 | 1.3266 | 1.3502 | N121-Mn1-N221 | 70.90 | 73.74 |
| C11-O21 | 1.2708 | 1.2626 | N111-Mn1-N121 | 97.85 | 99.03 |
| O31-H1W1 | 1.1561 | 1.0041 | N111-Mn1-N221 | 85.54 | 89.08 |
| O11-C11-O21 | 123.27 | 120.87 | N211-Mn1-N121 | 165.53 | 163.88 |
| O31-C111-O41 | 124.88 | 122.88 | N211-Mn1-N221 | 97.02 | 90.25 |

Table S5 Calculated Mulliken charges of the selected atoms in complex 17 and its oxidized state in atomic units (a.u.). Atom labeling scheme is in accordance with Figure 3 (see Article).

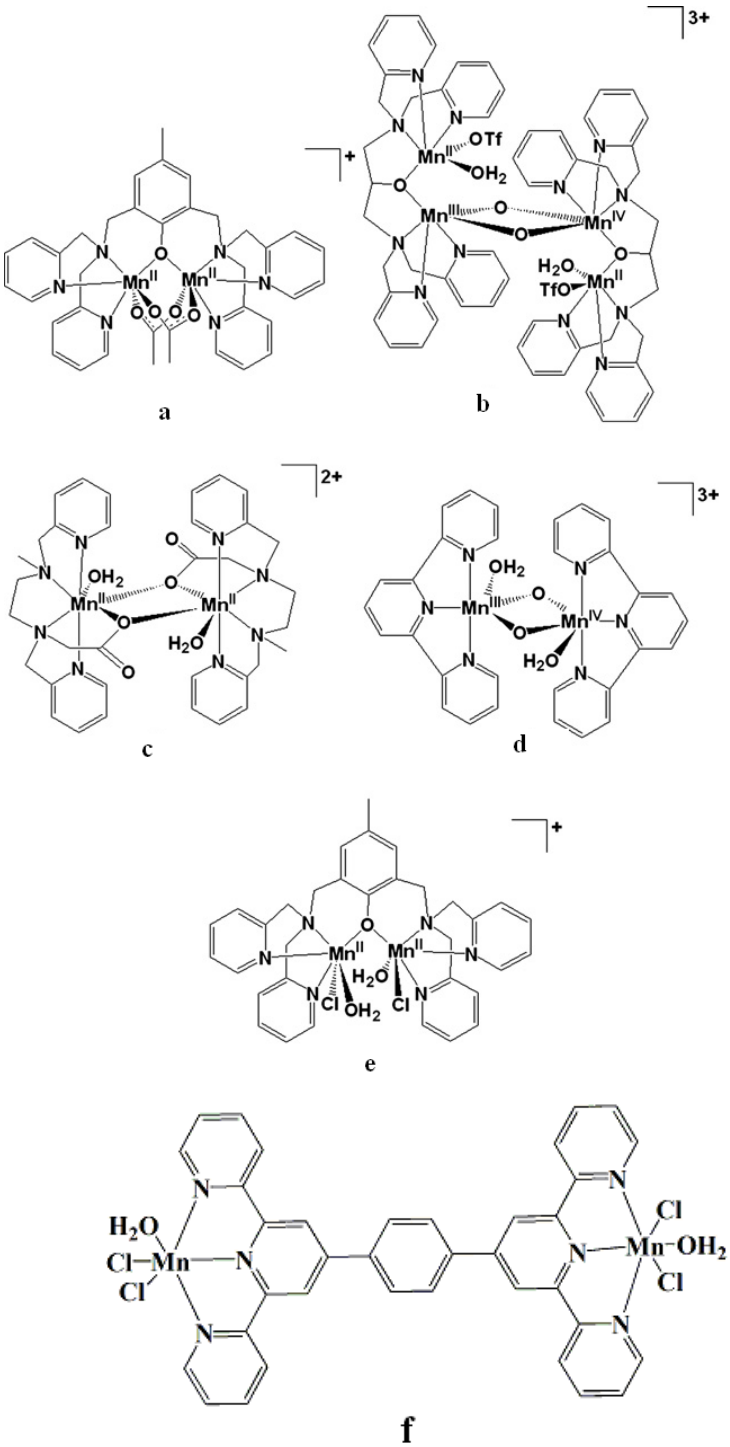
| Center | Mn(II) | Mn(III) | Center | Mn(II) | Mn(III) |
|---|---|---|---|---|---|
| Mn1 | 0.8454 | 0.8555 | O11 | -0.5404 | -0.5019 |
| O1W | -0.8479 | -0.7018 | C11 | 0.2040 | 0.2401 |
| H1W1 | 0.4626 | 0.4492 | O21 | -0.3628 | -0.3250 |
| H1W2 | 0.3505 | 0.3850 | N111 | -0.1916 | -0.3273 |
| O31 | -0.5146 | -0.4973 | N211 | -0.2495 | -0.3062 |
| C111 | 0.1325 | 0.1141 | N121 | -0.2382 | -0.2635 |
| O41 | -0.3592 | -0.2907 | N221 | -0.1589 | -0.2442 |

Table S6 Calculated pure spin values [α(↑)-β(↓)] for the selected atoms in complex 17 and its oxidized state.

| Center | Mn(II) | Mn(III) | Center | Mn(II) | Mn(III) |
|---|---|---|---|---|---|
| Mn1 | 4.8266 | 3.9038 | O11 | 0.0379 | 0.0171 |
| O1W | 0.0421 | -0.0070 | C11 | -0.0045 | -0.0010 |
| H1W1 | 0.0000 | 0.0014 | O21 | 0.0105 | 0.0079 |
| H1W2 | 0.0075 | 0.0116 | N111 | 0.0149 | -0.0435 |
| O31 | 0.0007 | 0.0010 | N211 | 0.0110 | 0.0303 |
| C111 | -0.0001 | -0.0003 | N121 | 0.0144 | 0.0446 |
| O41 | 0.0003 | 0.0011 | N221 | 0.0143 | 0.0134 |




Scheme S1. Structures of some Mn complexes used in the paper.




Scheme S2. Structure of the a-f complexes reported in Table 2 (see Article).

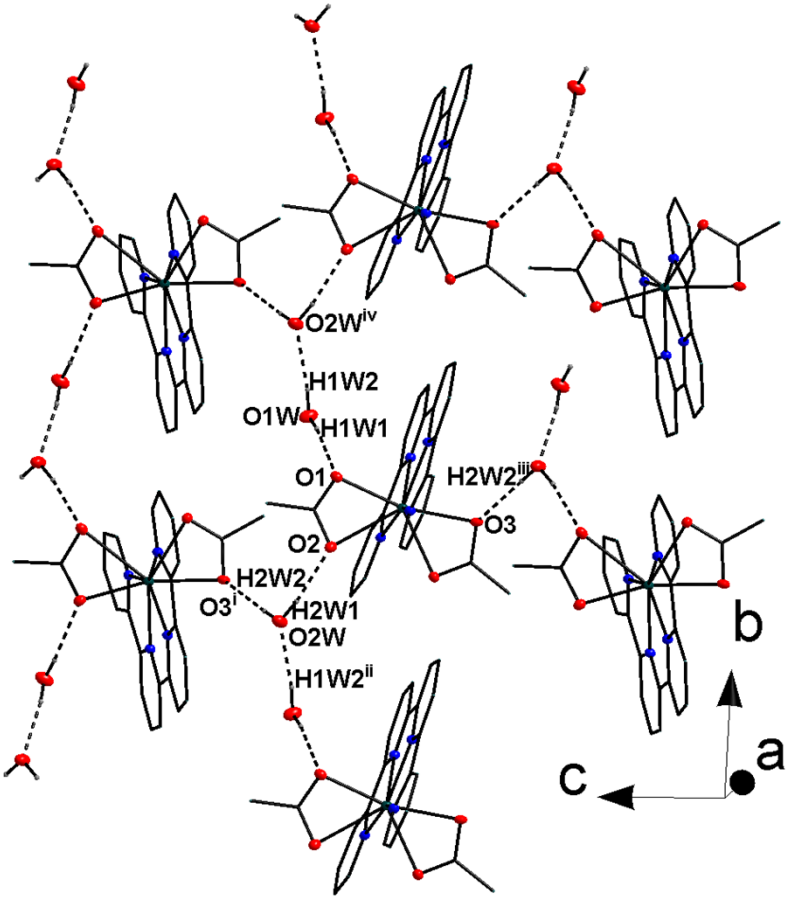



Fig. S1. Formation of a hydrogen-bonded layer in 15. Only H atoms involved in hydrogen bonding (dashed lines) are introduced. C atoms are shown as sticks. Thermal ellipsoids are plotted at 30% probability level. Symmetry codes: (i) x, 0.5-y, 0.5+z; (ii) x, y-1, z; (iii) x, 0.5-y, z-0.5; (iv) x, 1+y, z.

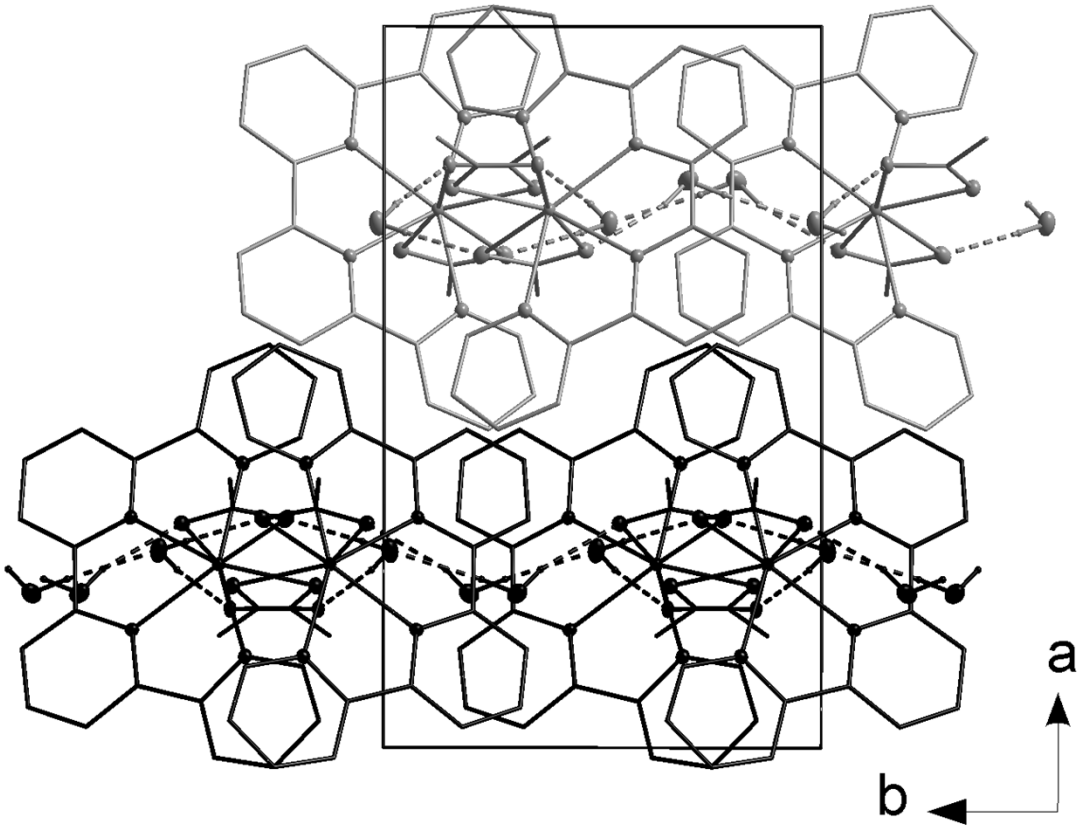
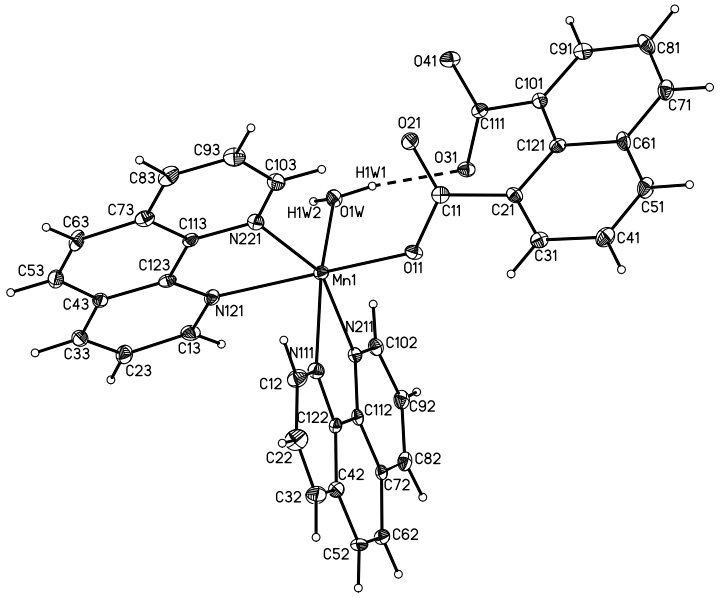
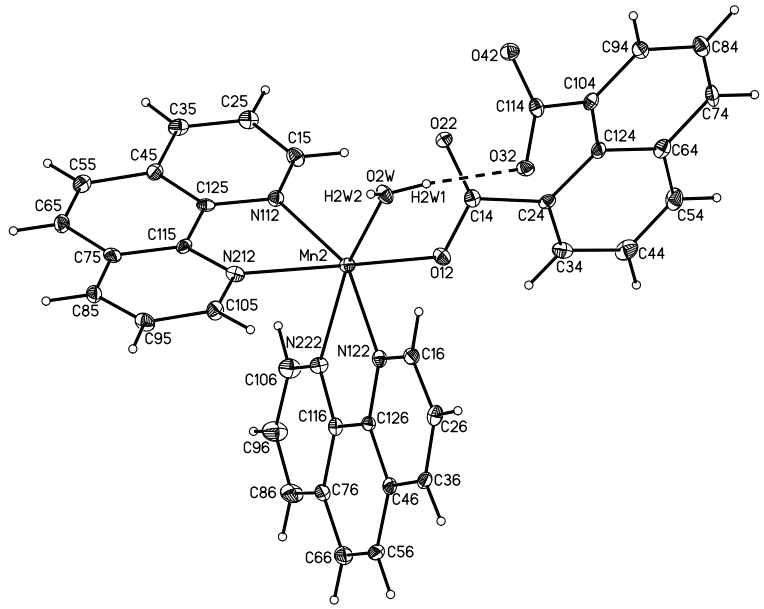


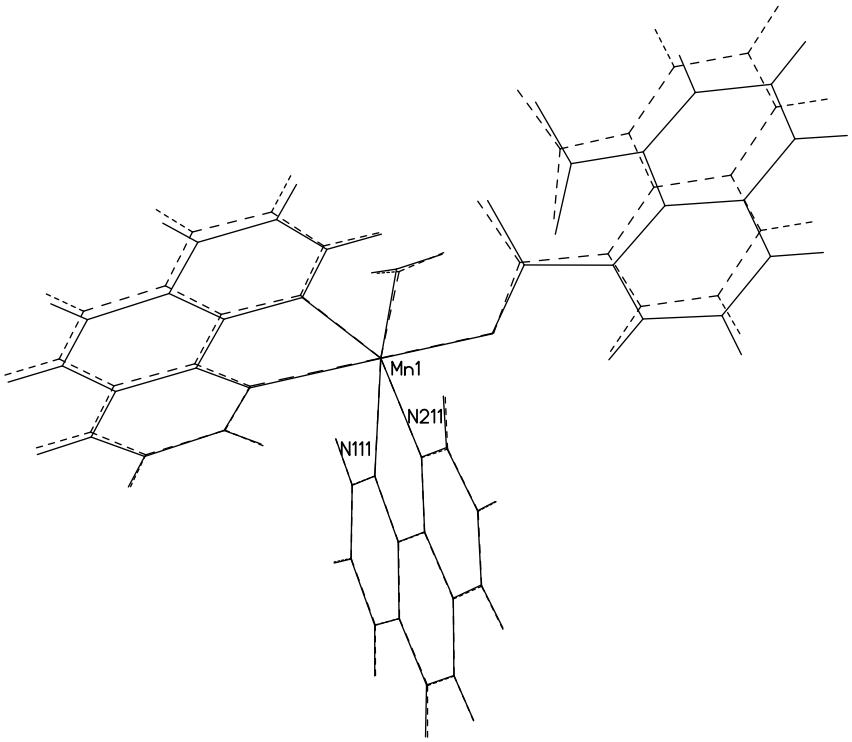

Fig. S2. Hydrogen-bonded layers in **15** parallel to (011). The two neighbouring layers are highlighted with different colours. Only H atoms involved in hydrogen bonding are shown. C atoms are denoted as sticks, thermal ellipsoids are plotted at 30% probability level, hydrogen bonding is shown with dashed lines.


O41
C91
C81
C101
C71
O21
C111
C121
C61
C93
C103
O31
H1W1
C83
H1W2
O1W
C11
C21
C51
C63
C73
C113
N221
C31
C41
C53
C123
Mn1
O11
C43
N121
N211
C102
C33
C13
N111
C23
C12
C112
C92
C122
C22
C82
C42
C72
C32
C62
C52

(a)

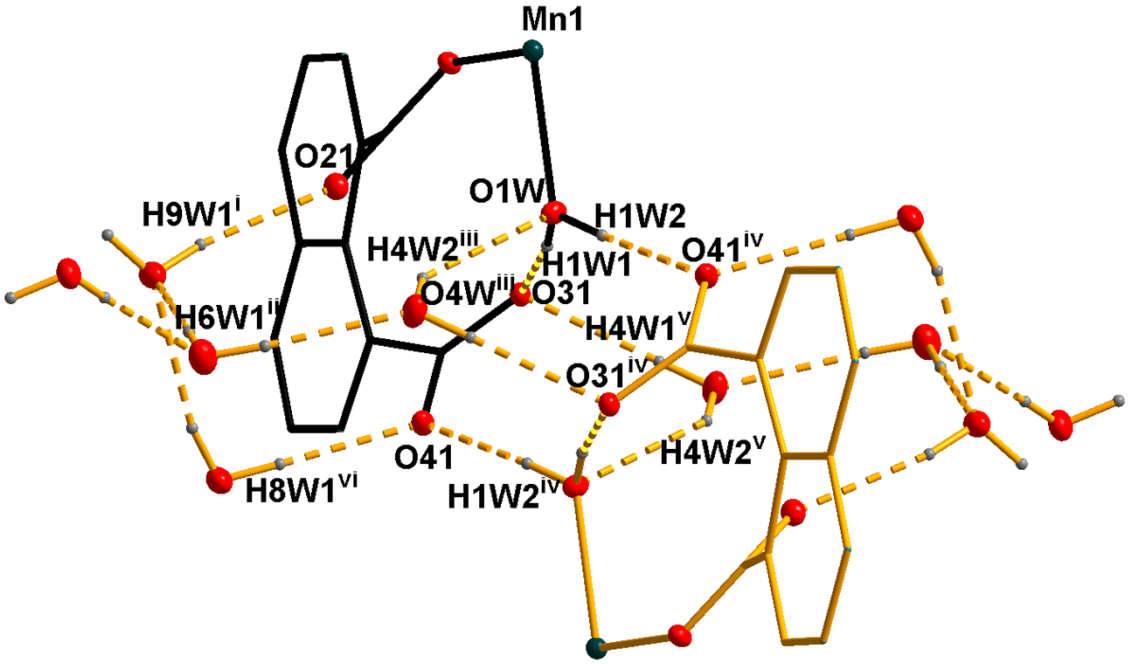

O42
C94
C84
C104
C114
C74
C35
C25
O22
C124
C15
C64
C45
O32
C55
O2W
C125
H2W2
H2W1
C65
N112
C14
C24
C54
C115
C75
N212
Mn2
O12
C34
C44
C85
C105
C95
N222
N122
C16
C106
C116
C126
C26
C96
C36
C86
C76
C46
C66
C56

(b)

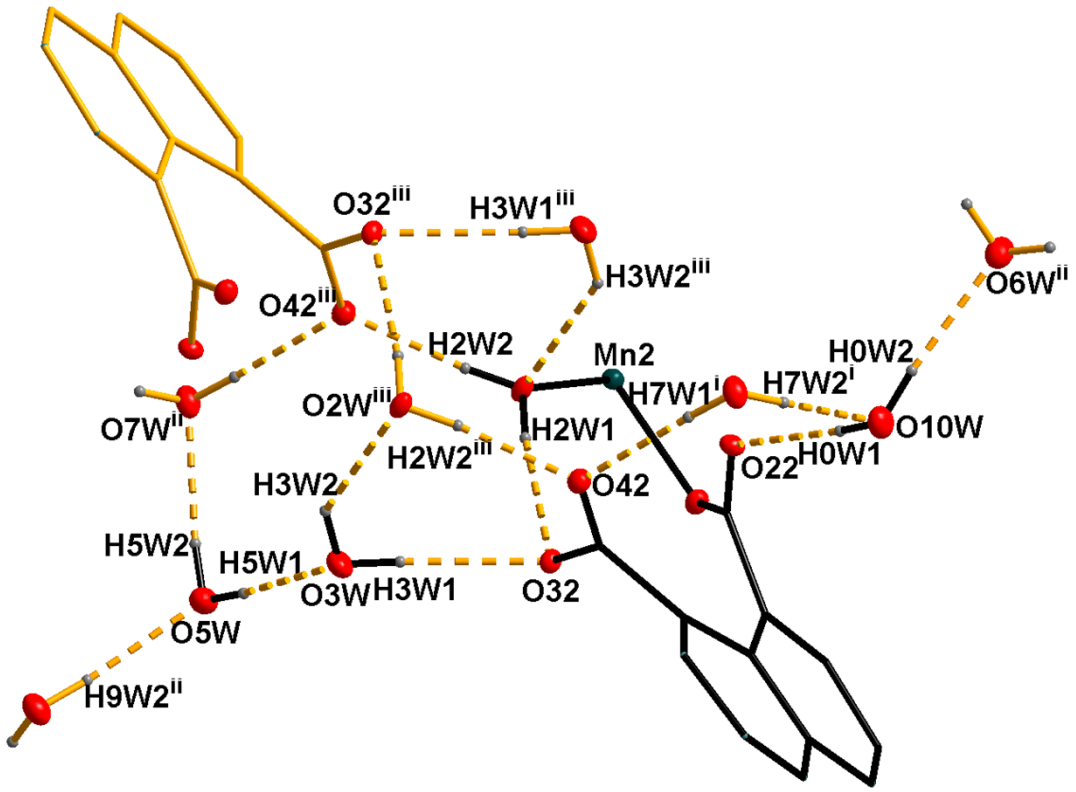



(c)

Fig. S3. (a)-(b) Molecular structure of the two symmetry-independent complex molecules **A** (a) and **B** (b) in **17**. Thermal ellipsoids are plotted at 30% probability level. H atoms are shown as spheres of arbitrary radii. Intramolecular hydrogen bonding is shown with dashed lines. (c) Overlap diagram of the two independent complex molecules. The fitted atoms are labeled.


Mn1
O21
O1W
H1W2
H9W1$^{i}$
H4W2$^{iii}$
H1W1
O41$^{iv}$
O4W$^{iii}$
O31
H6W1$^{ii}$
H4W1$^{v}$
O31$^{iv}$
O41
H4W2$^{v}$
H8W1$^{vi}$
H1W2$^{iv}$

(a)




(b)

Fig. S4. Hydrogen-bonded (dashed lines) cluster motif present in chains formed by the two independent molecules (compound **17**). C atoms are shown as sticks. Thermal ellipsoids are plotted at 30% probability level. The symmetry-independent part is highlighted in black. Symmetry codes: (a) [i] x, 1+y, z; [ii] –x, 2-y, 1-z; [iii] x-1, y, z; [iv] –x, 2-y, -z; [v] 1-x, 2-y, -z; [vi] x-1, 1+y, z; (b) [i] 1+x, y, z; [ii] 1-x, 1-y, 1-z; [iii] 2-x, 1-y, 1-z.

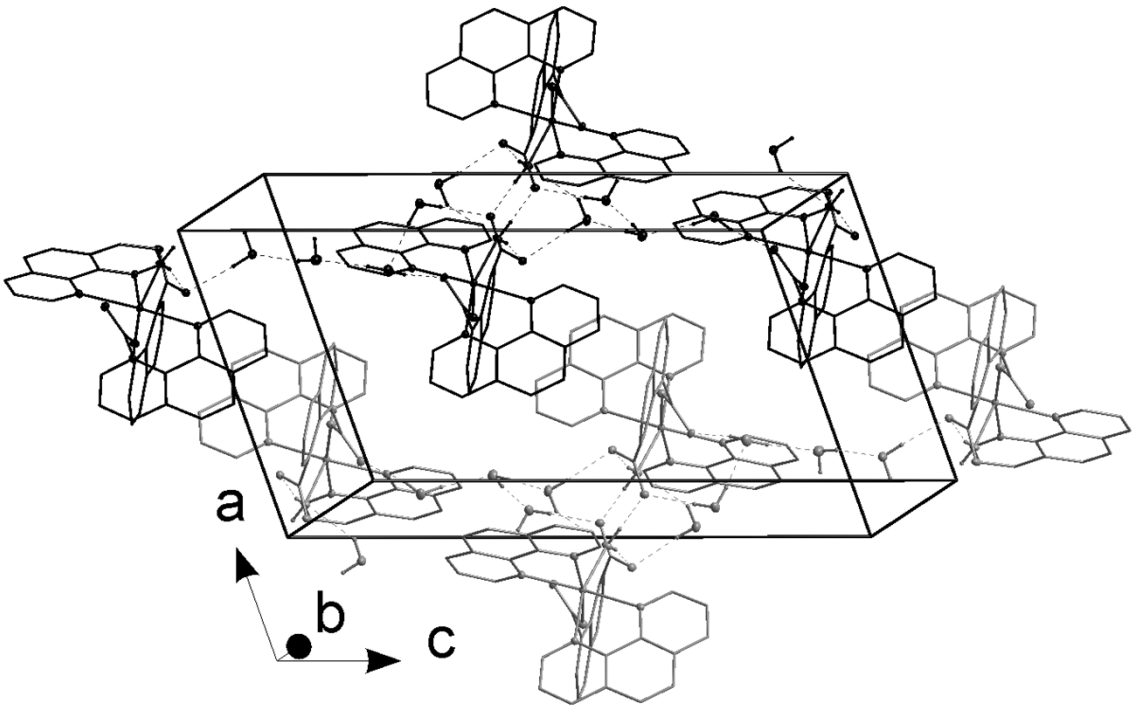



Fig. S5. Two neighbouring hydrogen-bonded (dashed lines) chains with hydrogen-bonded cluster motifs in **17**, denoted with different colours. Only H atoms involved in hydrogen bonding are visualized. C atoms are shown as sticks. Thermal ellipsoids are plotted at 30% probability level.

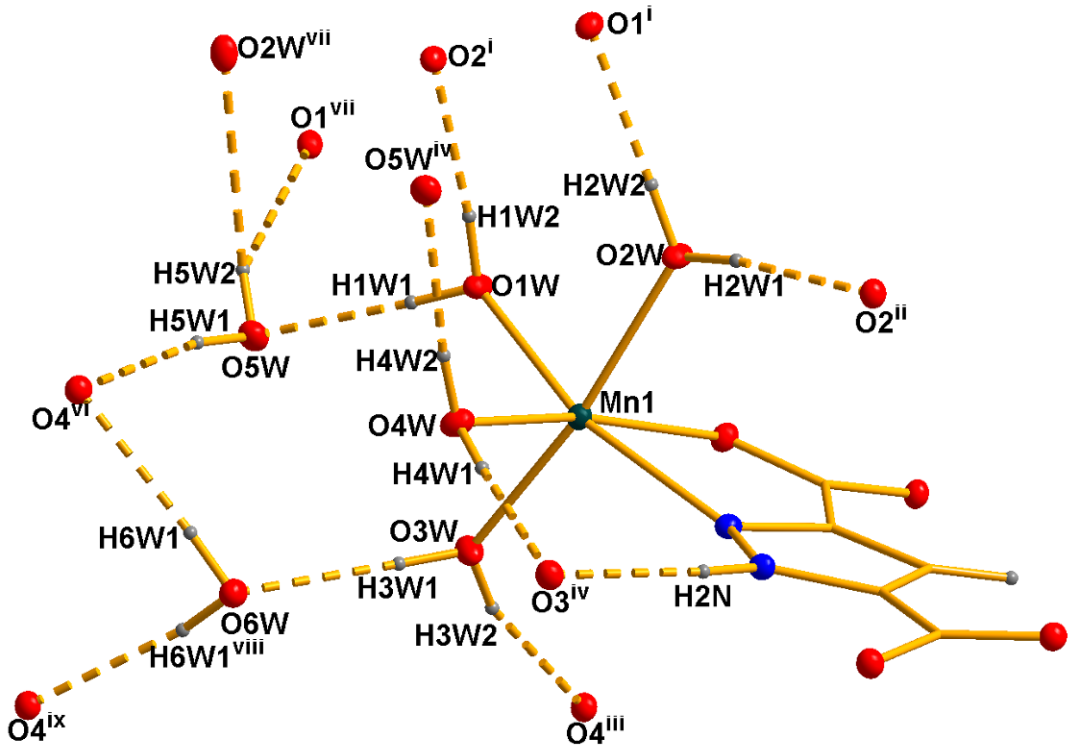



Fig. S6**.** Hydrogen bonding (dashed lines) scheme in **18**. H atoms are shown as spheres of arbitrary radii. C atoms are denoted as sticks. Thermal ellipsoids are plotted at 30% probability level. Symmetry codes: (i) -x+3/2, -y+3/2, z-1/2; (ii) x, -y+2, z-1/2; (iii) x, -y+2, z+1/2; (iv) -x+1, -y+2, -z; (v) x, -y+1, z-1/2; (vi) x, y-1, z; (vii) -x+3/2, y-1/2, z; (viii) 1-x, y, 0.5-z; (ix) 1-x, y-1, 0.5-z.

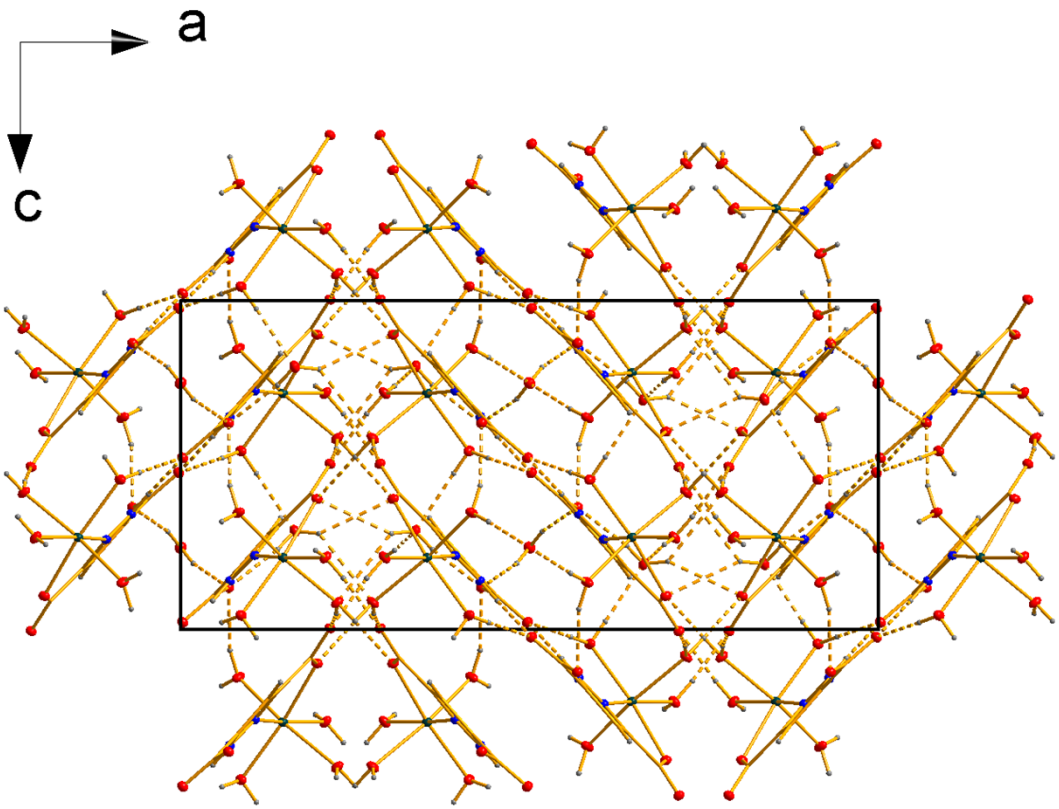



Fig. S7. View of the three-dimensional hydrogen-bonded network in **18** – projection along [010]. C atoms are shown as sticks, H atoms are denoted as spheres of arbitrary radii. Thermal ellipsoids are plotted at 30% probability level. Hydrogen bonds are shown as dashed lines.

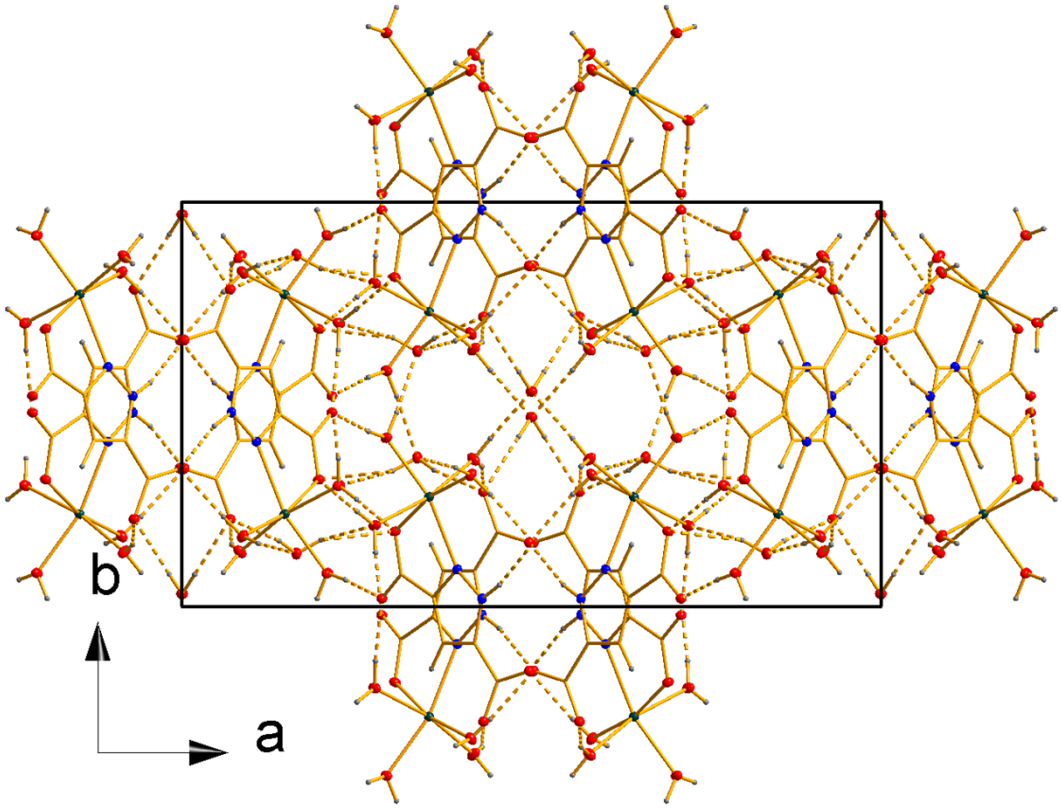



Fig. S8. View of the three-dimensional hydrogen-bonded network in **18** – projection along [001]. C atoms are shown as sticks, H atoms are denoted as spheres of arbitrary radii. Thermal ellipsoids are plotted at 30% probability level. Hydrogen bonds are shown as dashed lines.

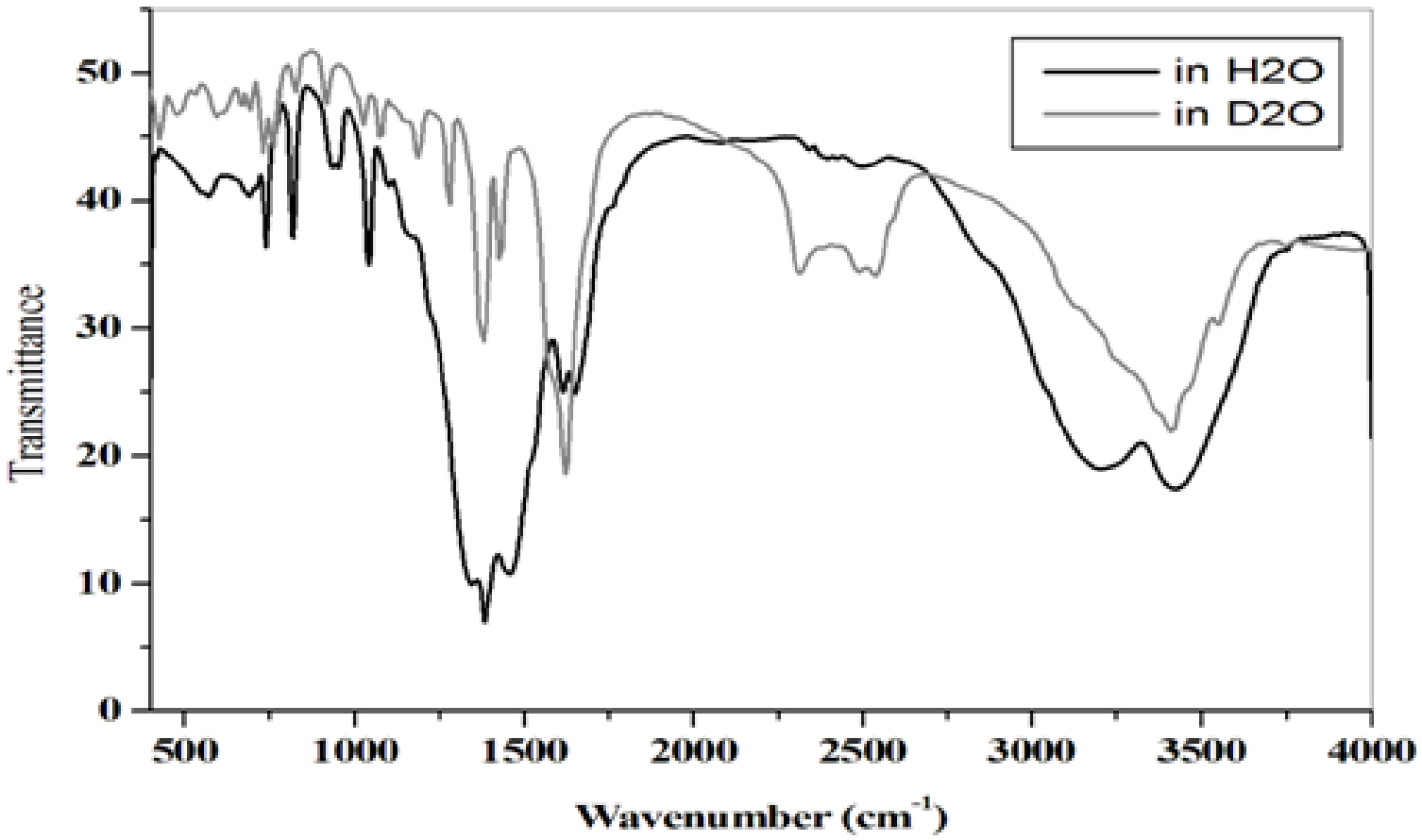



Fig. S9. IR spectrum of **9** and deuterated **9** at 500-4000 $cm^{-1}$.

(a)

(b)

Fig. S10. EPR spectra of many Mn(II) complexes with N and carboxylate groups (a), and in the presence of Oxone (b).

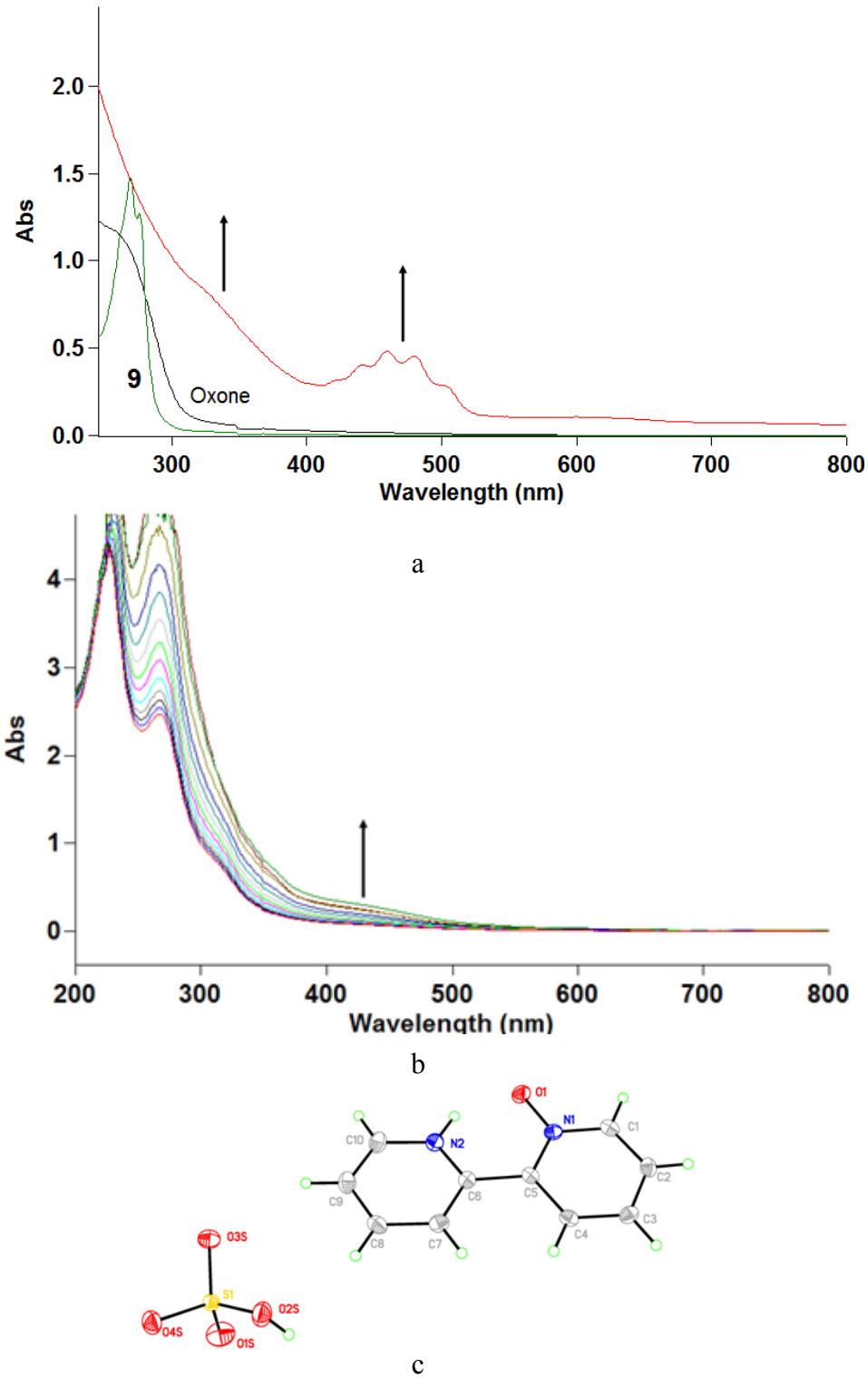
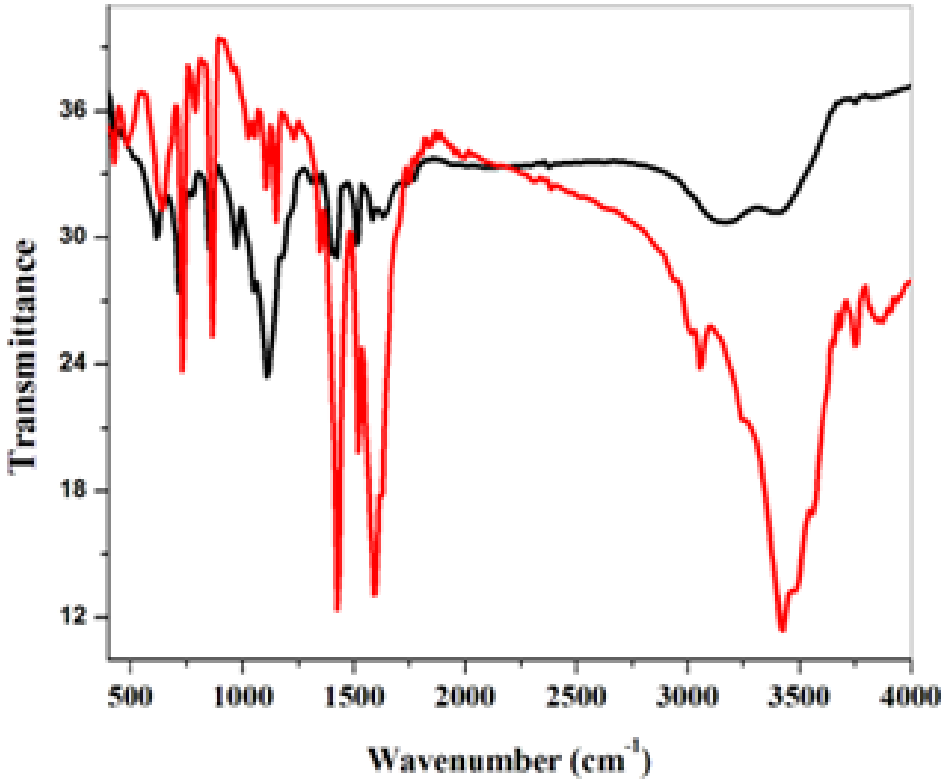
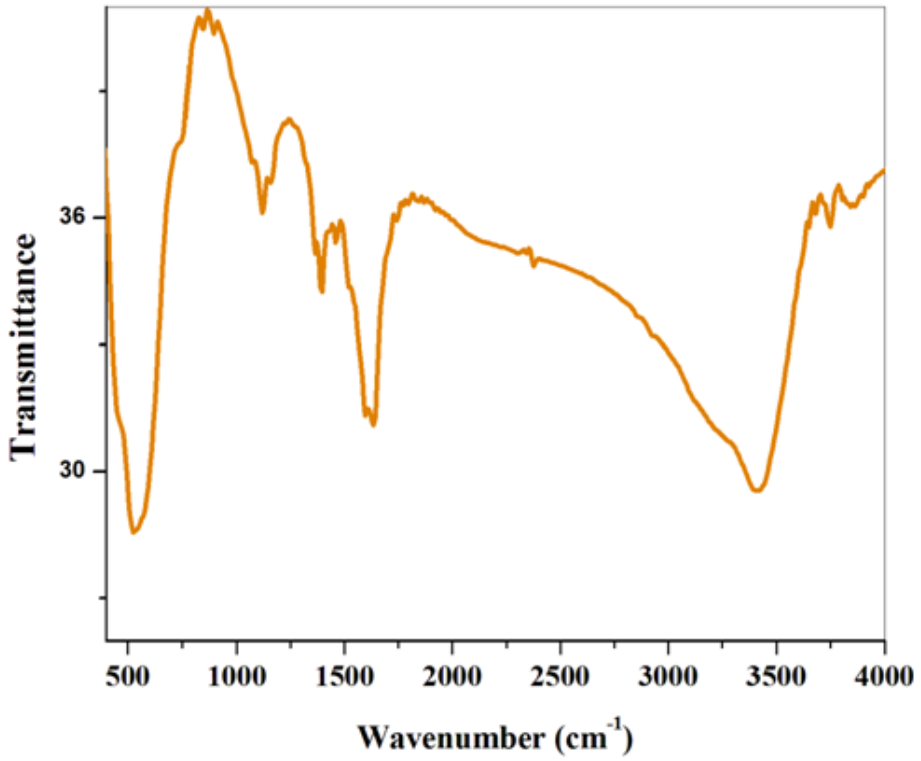



Fig. S11. The transient absorptions derived from **9** (0.2 mM) in water and the transient absorptions derived from mixing **9** (1 ml, 0.2 mM) and Oxone (1 ml, 1 mM) at pH= 4.5. Visible absorption spectra showing the reaction between **9** and Oxone to form $MnO_4^-$ ($\lambda_{max}$ = 520 nm). Arrows show the direction of absorbance change when adding Oxone

(a). The transient absorptions are derived for mixing of **5** (1 ml, 1.0 mM) and Oxone (0.5 ml, 5 mM). The arrows show the direction of absorbance change when adding Oxone (b). ORTEP plot of the structure of an oxidized bpy ligand salt obtained from the reaction of the Mn-bpy complex and Oxone[91] (c).

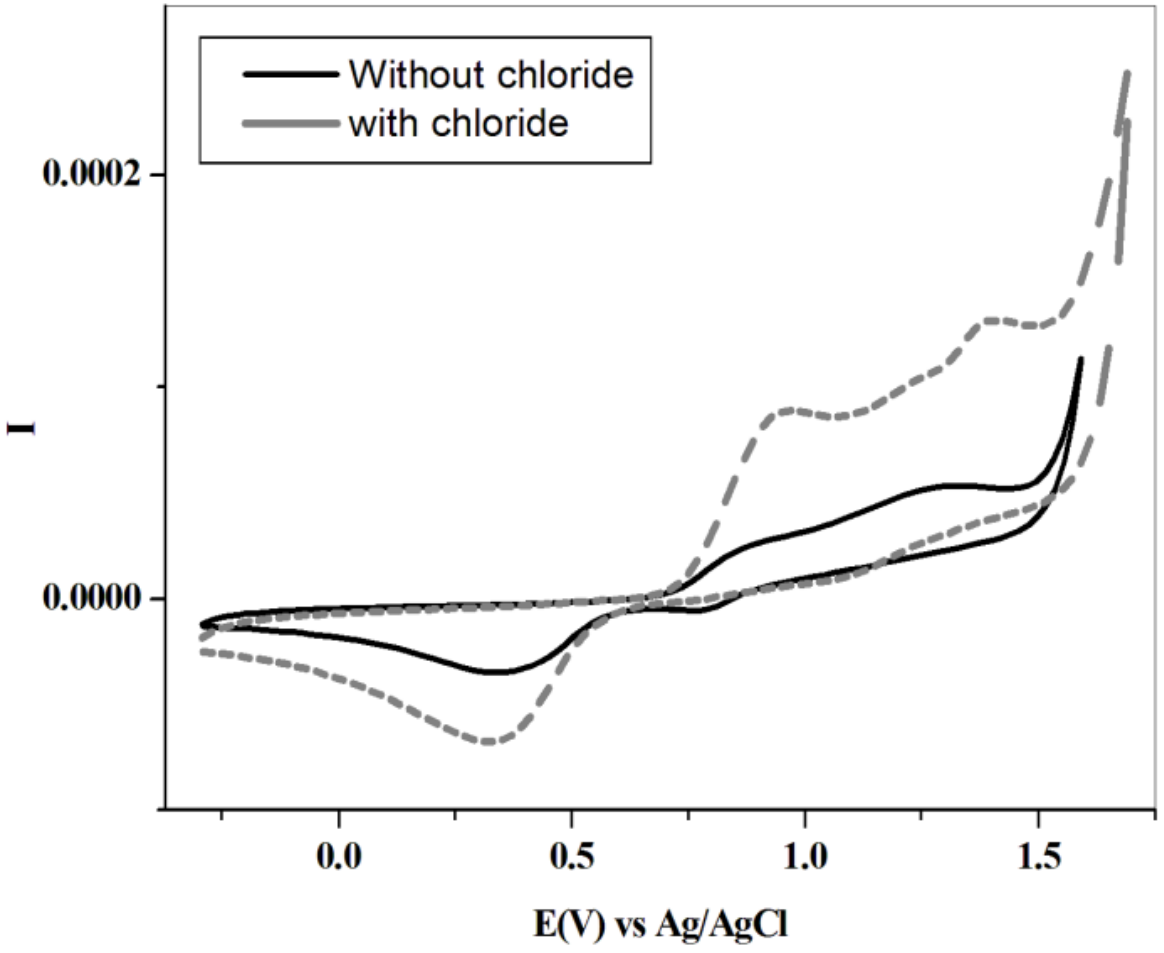

Transmittance
36
30
24
18
12
500
1000
1500
2000
2500
3000
3500
4000
Wavenumber (cm-1)

a

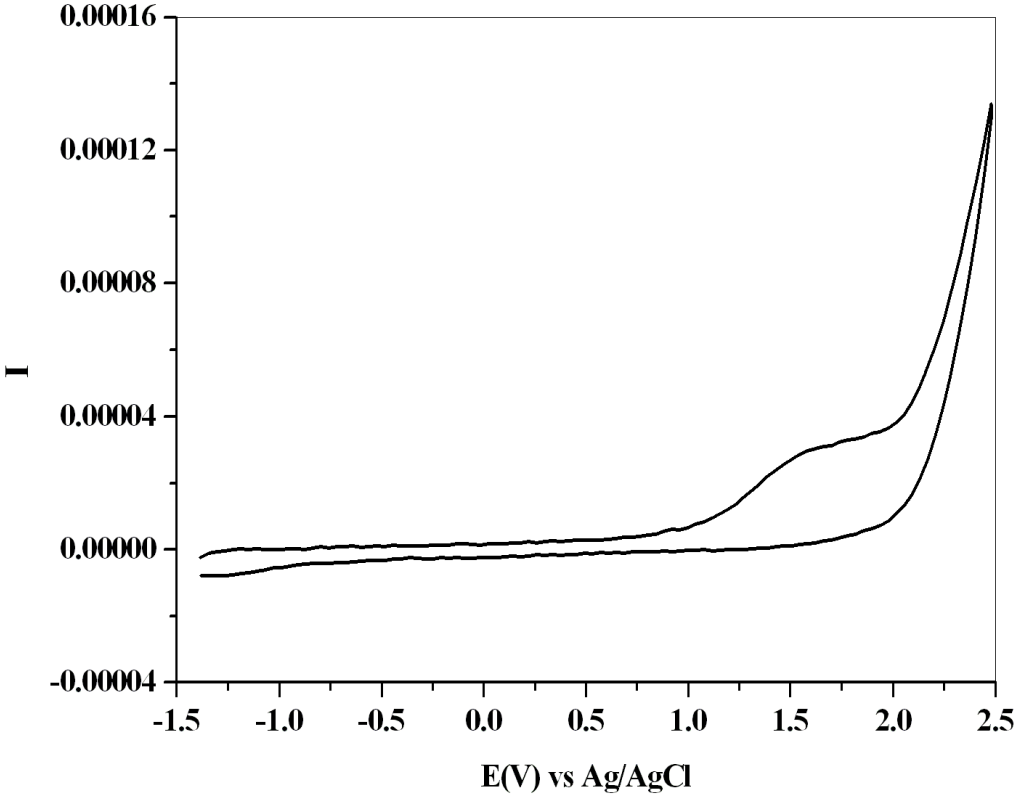

Transmittance
36
30
500
1000
1500
2000
2500
3000
3500
4000
Wavenumber (cm-1)

b

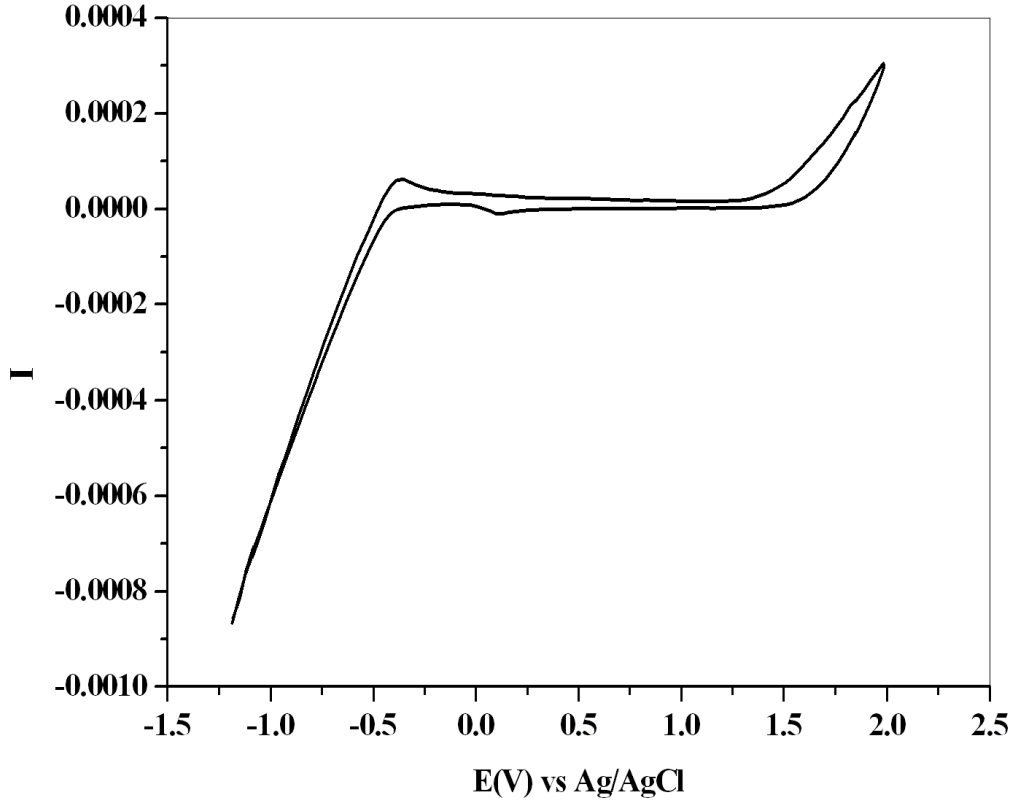
Fig. S12. IR spectra of **15** before (red) and after (black) reaction with Oxone (a). IR spectra of **10** after reaction with Oxone (b).


Without chloride
with chloride
0.0002
0.0000
I
0.0
0.5
1.0
1.5
E(V) vs Ag/AgCl

a

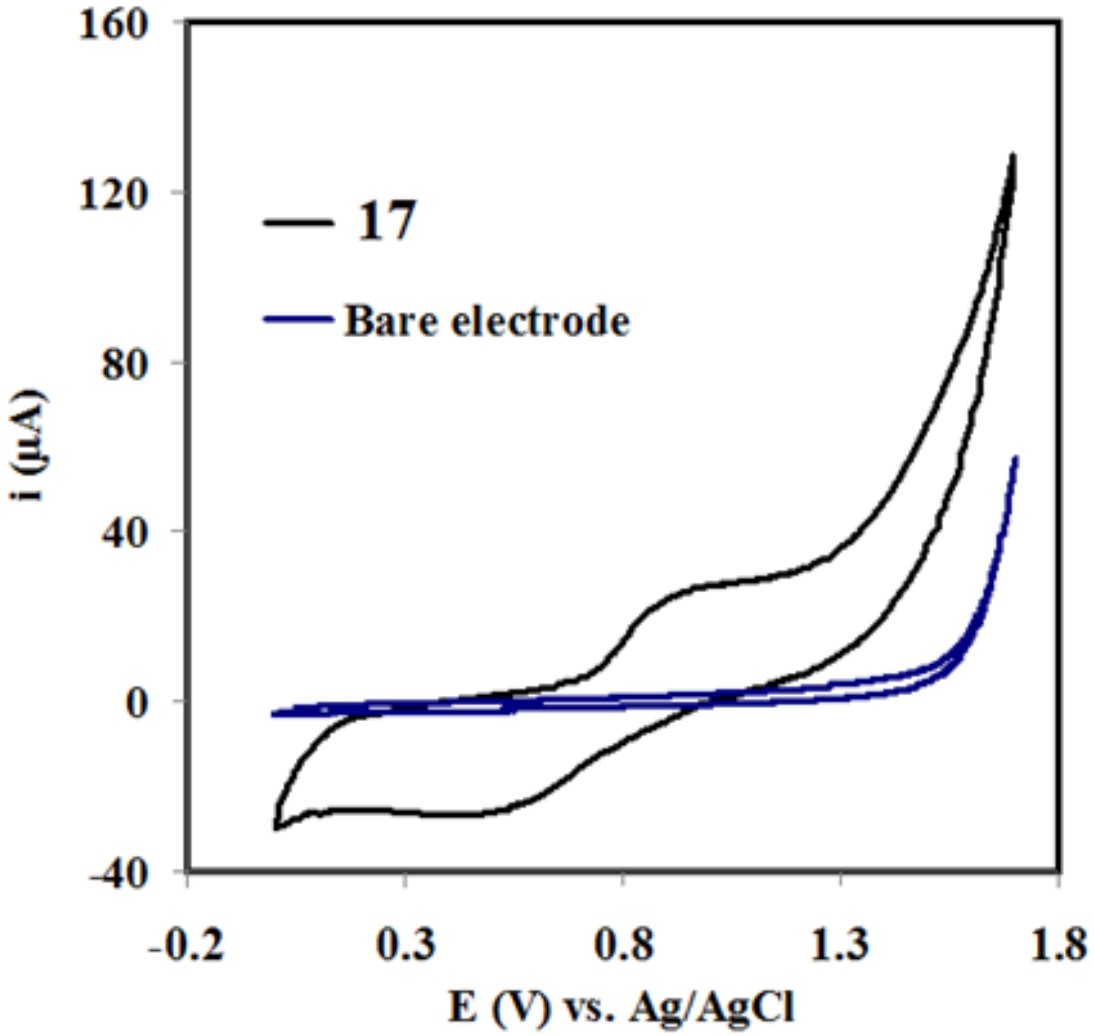

0.00016
0.00012
0.00008
0.00004
0.00000
-0.00004
I
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
2.5
E(V) vs Ag/AgCl

b

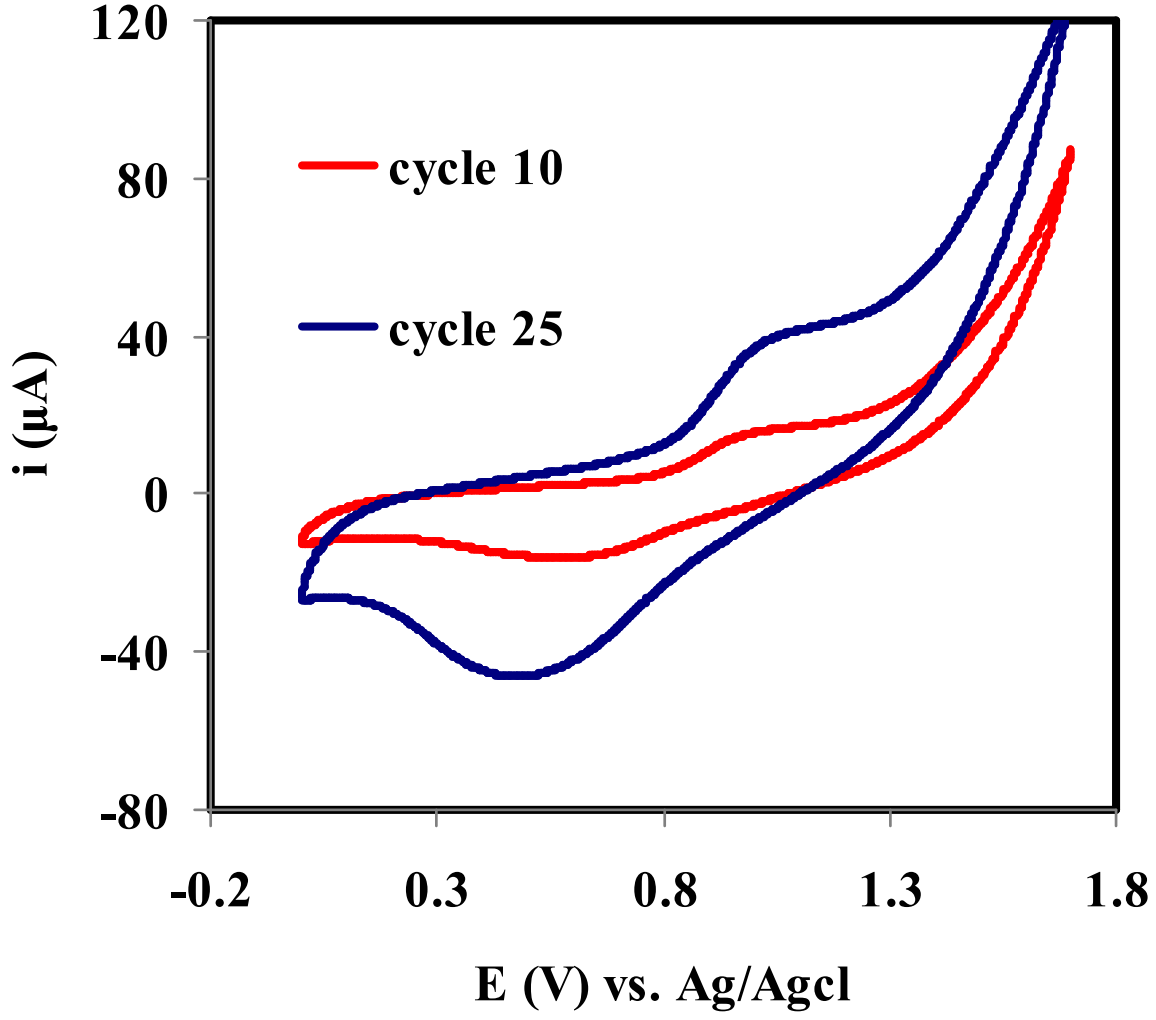



c

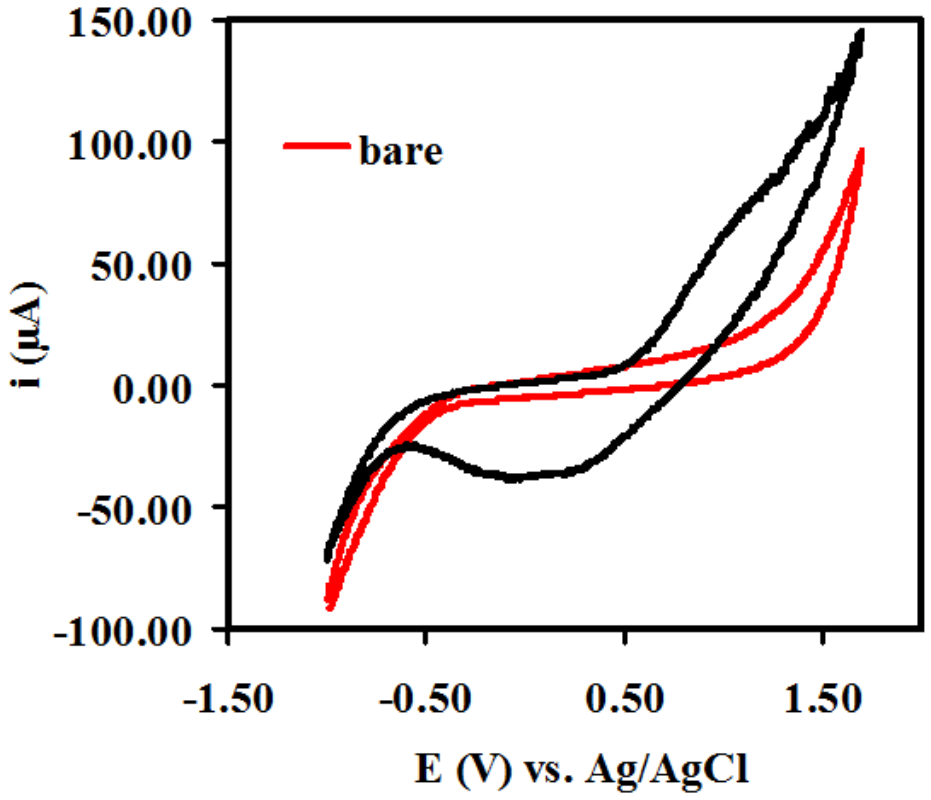
Fig. S13. Cyclic voltammograms in aqueous buffer at pH = 4.5 (scan rate 100 mV $s^{-1}$) of a 2 mM solution of **6** in the absence and in the presence of $Cl^-$ (a), **16** in acetonitrile (b) and water (c).


160
120
80
40
0
-40
i (µA)
17
Bare electrode
-0.2
0.3
0.8
1.3
1.8
E (V) vs. Ag/AgCl

a




b




c

Fig. S14. Cyclic voltammograms recorded for the bare carbon paste electrode (blue) and the carbon paste electrode containing **17** at a scan rate of 100 mV/s in an acetate buffer solution with pH = 5 (a). Succesive cyclic voltammograms (cycle number 10 and 25) recorded for the carbon paste electrode containing **16** at a scan rate of 100 mV/s in an acetate buffer solution of pH = 5 (b). Voltammetric behavior of **15** (black curve) dissolved in acetonitrile, containing 0.1 M of $LiClO_4$ as supporting electrolyte at a scan rate of 100 mV/s. Behavior of the glassy carbon electrode is provided for better comparison (red curve) (c).

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