Supplementary Material (ESI) for Dalton Transactions


# Supplementary information

## A novel asymmetric di-Ni(II) system as highly efficient functional model for phosphodiesterase: Synthesis, structures, physicochemical properties and catalytic kinetics

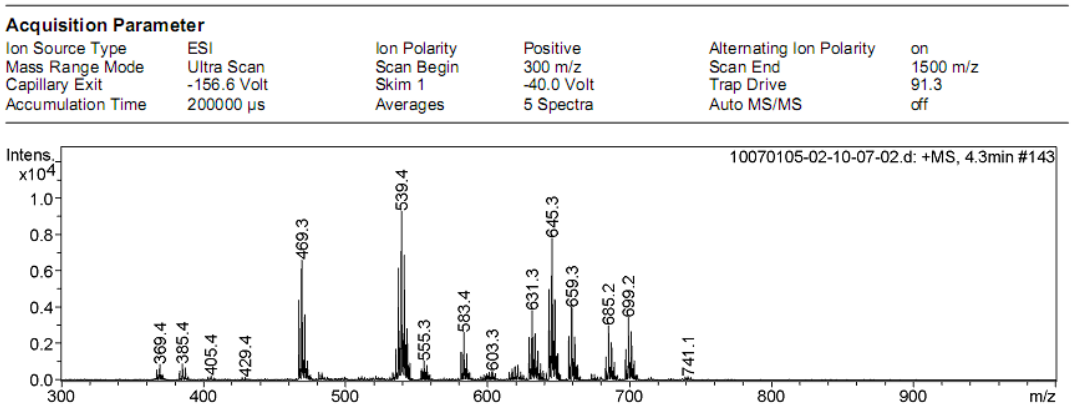
Yan-wei Ren[1], Jia-xian Lu[1], Bo-wei Cai[1], Da-bin Shi[1], Huan-feng Jiang[*1], Jun Chen[2], De Zheng[2], and Bin Liu[3]

**Table S1**. Crystal data and structure refinement for complexes **2** and **3**

| Complexes | **2** | **3** |
|---|---|---|
| Empirical formula | $C_{62}H_{64}BBrN_{10}Ni_2O_{13}$ | $C_{72}H_{78}BBrN_6Ni_2O_9P_2$ |
| Formula weight | 1365.32 | 1441.43 |
| Crystal size (mm) | 0.30 × 0.20 × 0.20 | 0.30 × 0.20 × 0.10 |
| T(K) | 293 | 293 |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | Monoclinic | Triclinic |
| Space group | $P2_1/c$ | $P$-1 |
| $a$(Å) | 13.222(3) | 14.913(3) |
| $b$(Å) | 25.914(5) | 15.245(3) |
| $c$(Å) | 19.506(4) | 15.720(3) |
| α(°) | 90 | 93.31(3) |
| $\beta$(°) | 107.11(3) | 99.98(3) |
| $\gamma$(°) | 90 | 90.46(3) |
| $V$(Å$^3$) | 6387(2) | 3513.5(12) |
| $Z$ | 4 | 2 |
| Density (g·cm$^{-1}$) | 1.414 | 1.356 |
| $F$ (000) | 2800 | 1486 |
| Absorption coefficient (mm$^{-1}$) | 1.285 | 1.210 |
| Data / restraints / parameters | 11227 / 6 / 803 | 12269 / 174 / 737 |
| $\theta$ range for data collection (°) | 3.07 to 25.00 | 3.01 to 25.00 |
| Reflections collected | 48779 | 27514 |
| Independent reflections | 11227 ($R_{int}$= 0.0837) | 12269 ($R_{int}$=0.1194) |
| GOF on $F^2$ | 1.013 | 1.054 |
| Final R indices[$I$>2σ($I$)] | $R_1$ = 0.0650<br>$wR_2$ = 0.1705 | $R_1$ = 0.0942<br>$wR_2$ = 0.2153 |
| $R$ indices (all data) | $R_1$ = 0.1333<br>$wR_2$ = 0.2095 | $R_1$ = 0.2450<br>$wR_2$ = 0.2942 |

**Table S2.** Selected Bond Lengths (Å) and Angles (deg) for complexes **2** and **3**

| **2** | | **3** | |
|---|---|---|---|
| Bond lengths (Å) | | | |
| Ni (1)-O(1) | 1.993(4) | Ni(1)-O(1) | 2.073(10) |
| Ni (1)-O(3) | 2.016(4) | Ni (1)-O(2) | 2.036(10) |
| Ni(1)-O(5) | 2.094(4) | Ni (1)-O(6) | 2.069(11) |
| Ni (1)-N(3) | 2.088(5) | Ni (1)-N(1) | 2.080(13) |
| Ni (1)-N(4) | 2.152(6) | Ni (1)-N(2) | 2.117(13) |
| Ni (1)-N(6) | 2.155(7) | Ni (1)-N(5) | 2.144(15) |
| Ni(2)-O(1) | 1.995(4) | Ni (2)-O(1) | 2.010(11) |
| Ni (2)-O(2) | 2.082(4) | Ni(2)-O(3) | 2.015(10) |
| Ni (2)-O(4) | 2.020(4) | Ni (2)-O(7) | 2.067(11) |
| Ni (2)-N(1) | 2.085(5) | Ni (2)-N(3) | 2.072(12) |
| Ni (2)-N(2) | 2.112(5) | Ni (2)-N(4) | 2.069(14) |
| Ni (2)-N(5) | 2.088(6) | Ni (2)-N(6) | 2.115(18) |
| Ni (1)$^{\cdots}$ Ni (2) | 3.445 | Ni (1)$^{\cdots}$ Ni (2) | 3.639 |
| Bond angles (deg) | | | |
| O(1)-Ni(1)-O(3) | 96.21(16) | O(2)-Ni(1)-O(1) | 91.5(4) |
| O(1)-Ni(1)-N(3) | 91.33(18) | O(1)-Ni(1)-N(1) | 92.4(5) |
| N(3)-Ni(1)-N(4) | 74.8(2) | N(1)-Ni(1)-N(2) | 75.6(6) |
| O(3)-Ni(1)-N(4) | 97.7(2) | O(6)-Ni(1)-N(2) | 97.0(5) |
| O(5)-Ni(1)-N(6) | 168.0(2) | O(2)-Ni(1)-N(5) | 172.9(5) |
| O(1)-Ni(2)-O(4) | 95.52(16) | O(1)-Ni(2)-O(3) | 94.0(4) |
| O(1)-Ni(2)-N(1) | 89.92(16) | O(1)-Ni(2)-N(3) | 93.3(5) |
| N(1)-Ni(2)-N(2) | 81.94(18) | N(3)-Ni(2)-N(4) | 82.5(5) |
| O(4)-Ni(2)-N(2) | 92.74(17) | O(3)-Ni(2)-N(4) | 90.4(5) |
| O(2)-Ni(2)-N(5) | 172.64(18) | O(7)-Ni(2)-N(6) | 177.0(6) |
| Ni(1)-O(1)-Ni(2) | 119.46 | Ni(1)-O(1)-Ni(2) | 126.09 |




| # | m/z | I | I % |
|---|---|---|---|
| 1 | 467.4 | 4374 | 47.1 |
| 2 | 469.3 | 6584 | 71.0 |
| 3 | 537.4 | 6141 | 66.2 |
| 4 | 539.4 | 9278 | 100.0 |
| 5 | 541.4 | 6849 | 73.8 |
| 6 | 631.3 | 3816 | 41.1 |
| 7 | 643.3 | 4965 | 53.5 |
| 8 | 645.3 | 7809 | 84.2 |
| 9 | 647.3 | 4414 | 47.6 |
| 10 | 659.3 | 3995 | 43.1 |

**Figure S3.** ESI-MS spectrum of complex 1. Solvent: water/ethanol (1/1, v/v)

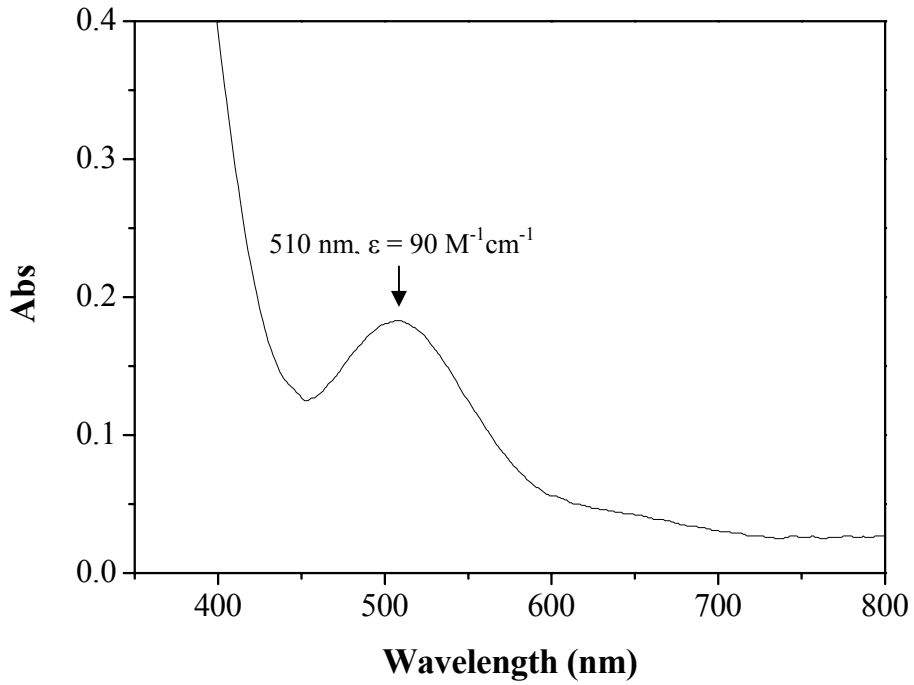



**Figure S4** UV-vis spectrum of complex 1. Solvent: water/ethanol (1/1, v/v)

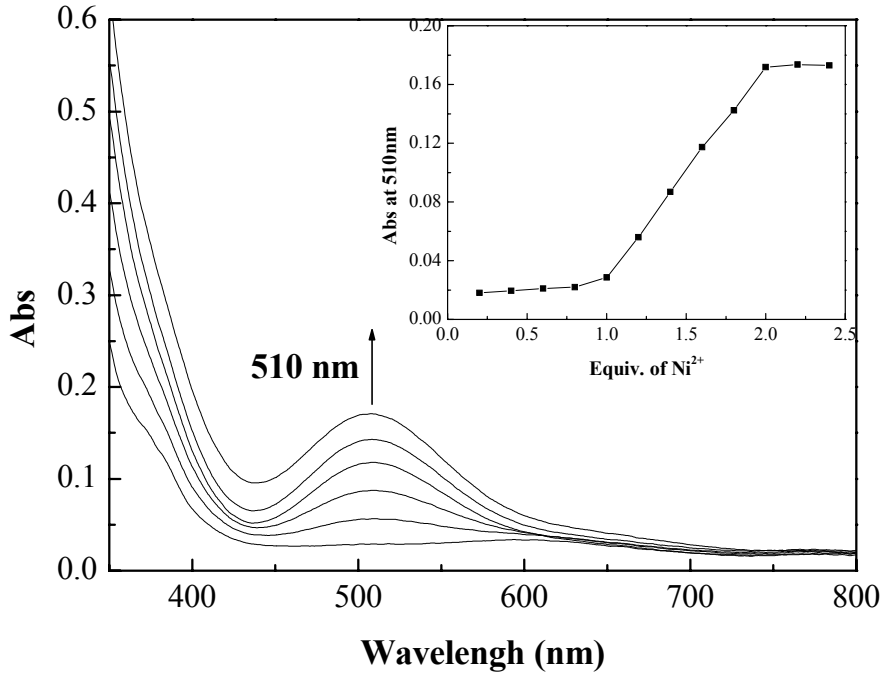



**Figure S5.** UV-vis spectra recorded upon titration of $Ni^{2+}$ to **HL** in buffer solution (50 mM HEPPS and 100 mM $NaClO_4$ in water/ethanol (1/1, v/v), pH = 8.3), Inset: absorbance at 510 nm vs. equivalent of $Ni^{2+}$ added.