Supplementary Information

Facile Formation & Redox of Benzoxazole-2-thiolate-Bridged Dinuclear Pt(II/III) Complexes

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Calculation Details

All DFT calculations were performed using the SIESTA package[1] with numerical atomic orbital basis sets and Troullier-Martins norm-conserving pseudopotentials. [2] The exchange-correlation functional utilized was GGA-PBE,[3] and the optimized double-ζ plus polarization (DZP) basis set was employed.

Structure of complex 1

Pt - Pt distance 3.055 Å, exp. 3.02 Å
From Mulliken charge analysis, the Pt - Pt overlap population is -0.036, indicating Pt - Pt is antibonding.
Ionization energy E=5.88 eV
Electron affinity = 1.03 eV

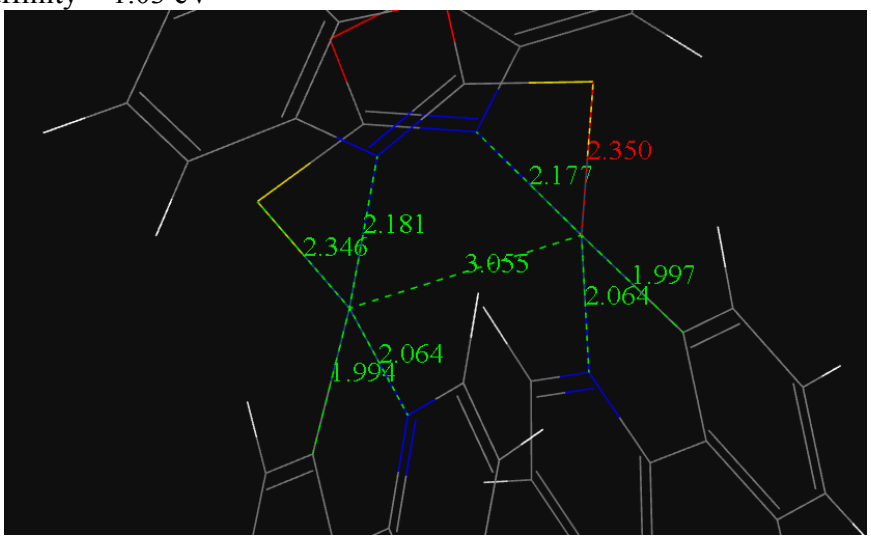


Figure 1. Complex **1**

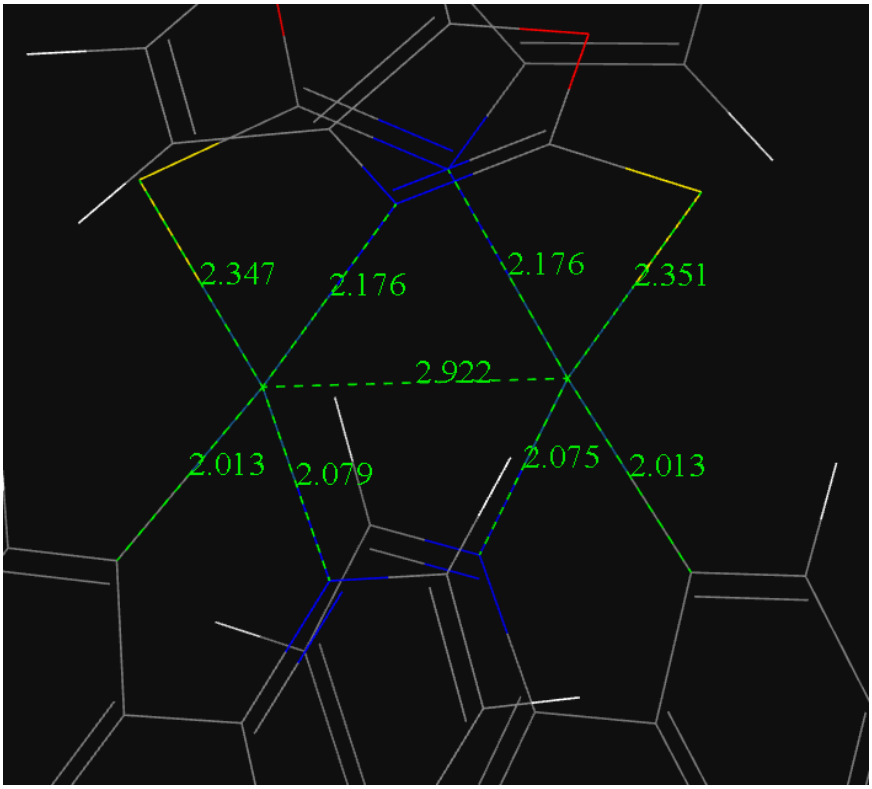


Figure 2. Complex **1** +1 charge.

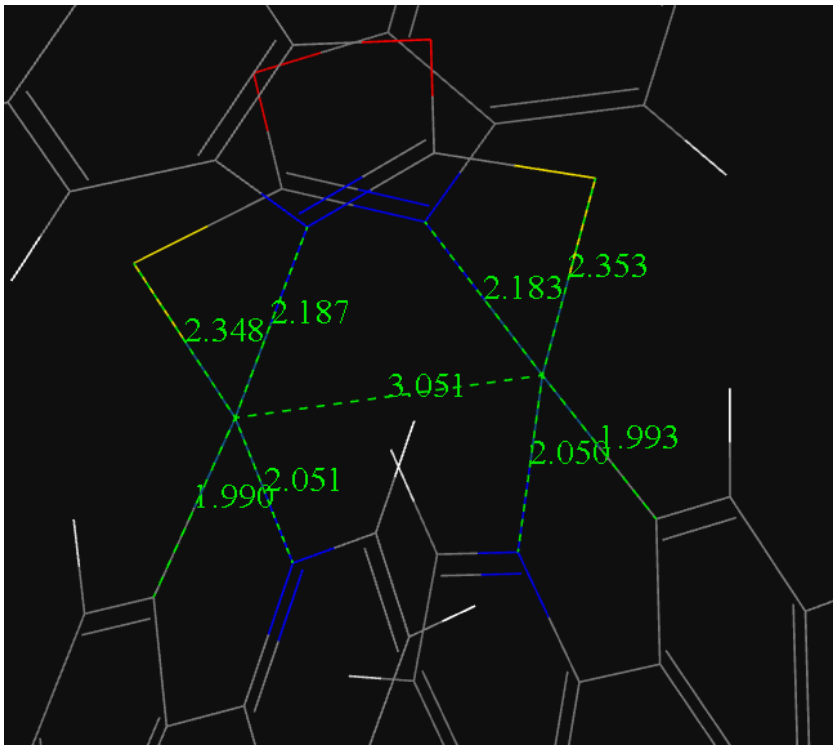


Figure 3. Complex **1** -1 charge.

Structure of complex 3

Neutral, E = -17204.7629, Pt-Pt distance 2.775 Å exp. 2.685 Å
From Mulliken charge analysis, Pt-Pt Overlap integral is 0.117, indicating there is Pt-Pt bonding formation.
Ionization energy = 5.96 eV
1st Electron affinity = 2.06 eV
2nd Electron affinity = 0.47 eV

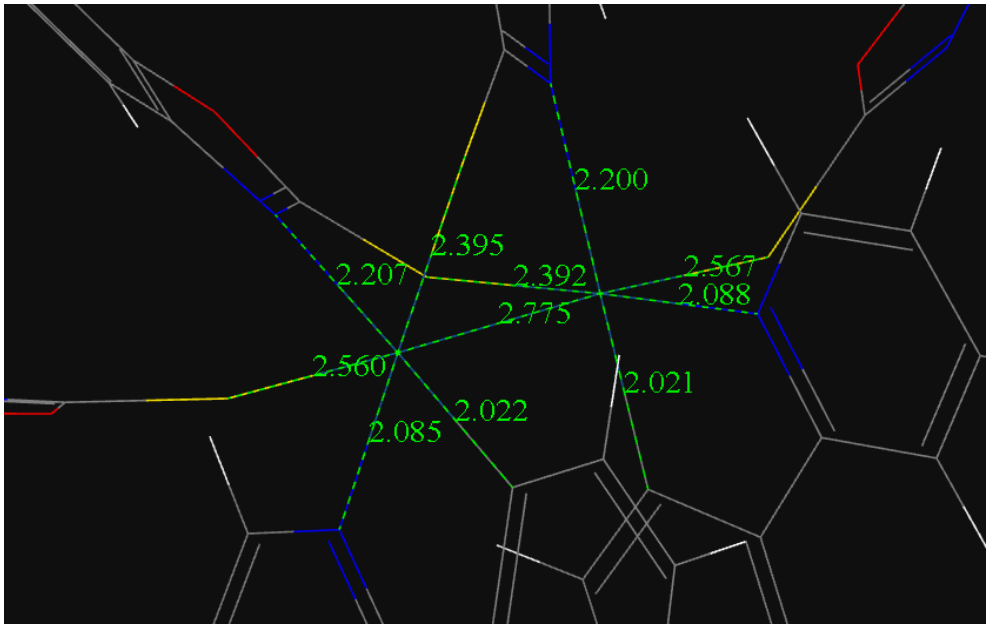


Figure 4. Complex **3**

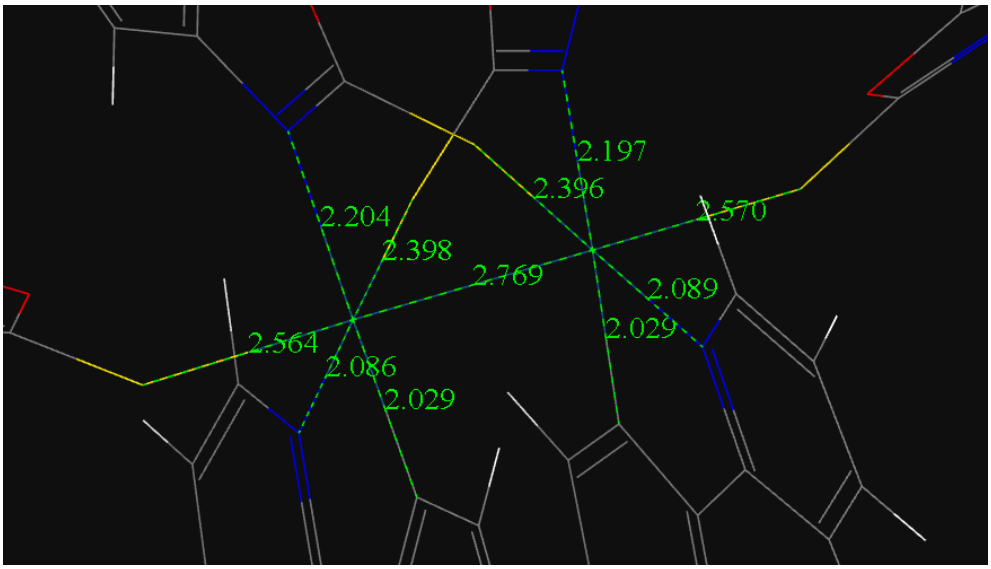


Figure 5. Complex **3** +1 charge.

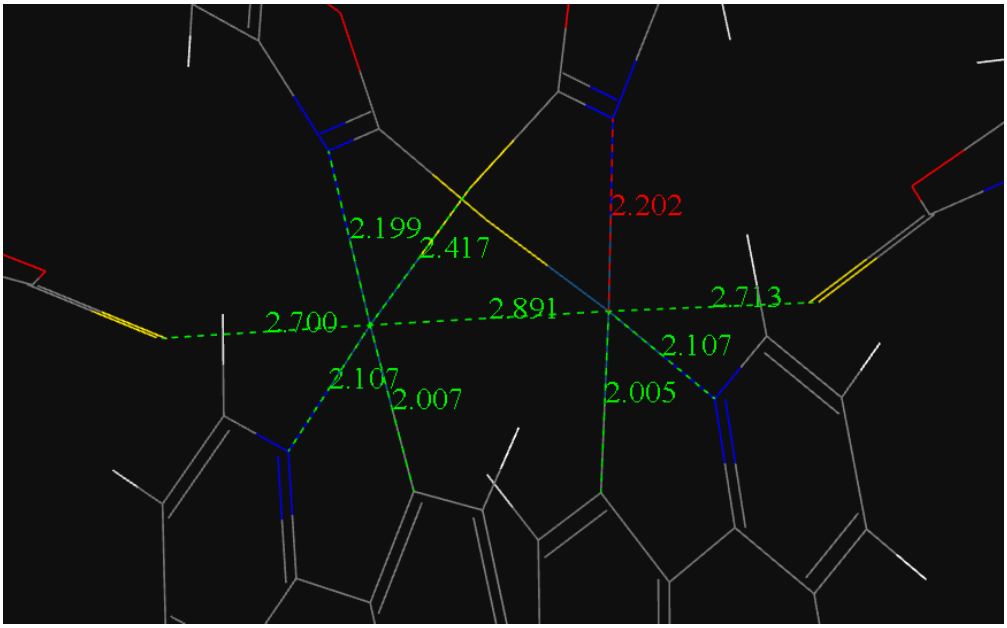


Figure 6. Complex **3** -1 charge.

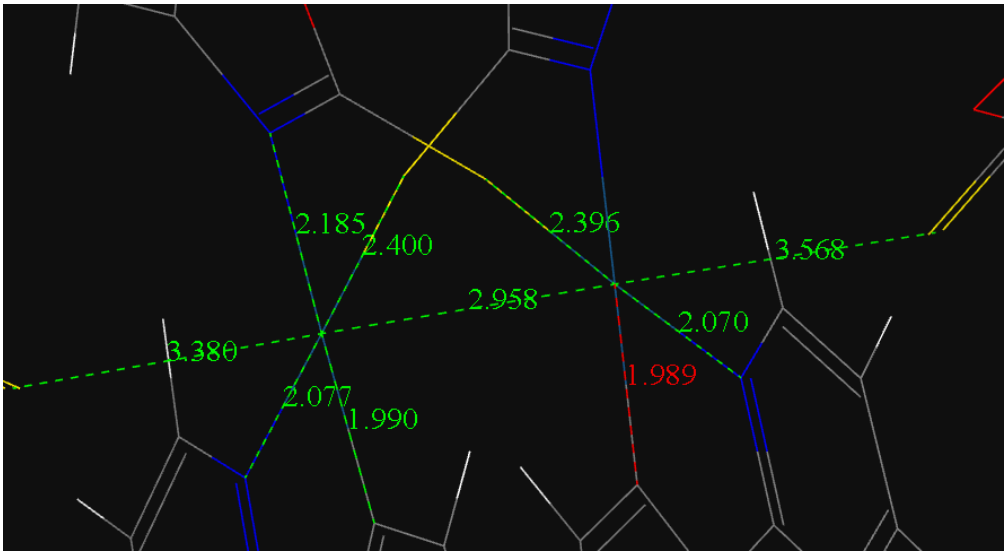
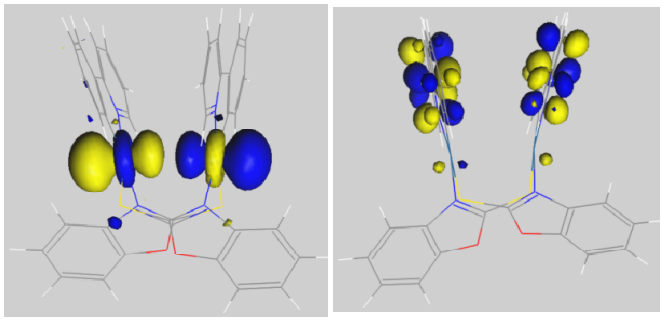


Figure 7. Complex **3** -2 charge.

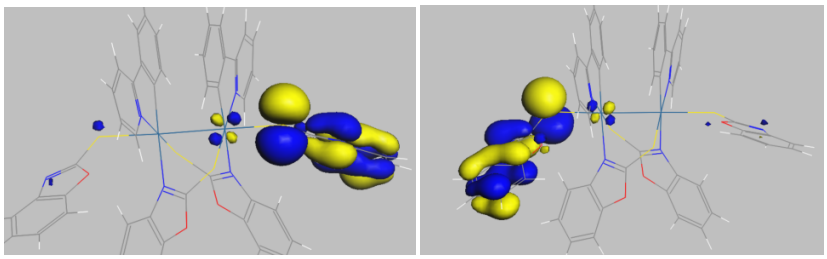
Molecular orbital of complex 1



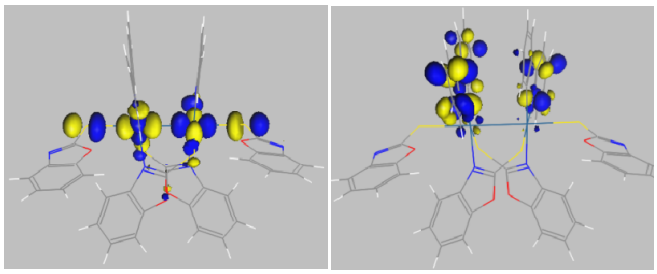
(a) (b)

Figure 8. (a) HOMO, energy = -4.11189 eV and (b) LUMO, energy = -2.56572 eV of complex **1**,

Molecular orbital of complex 3



(a) (b)



(c) (d)

Figure 9. (a) HOMO, energy = -4.55261 eV (b) HOMO -1, energy = -4.56666 eV (c) LUMO, energy = -3.31723 eV and (d) LUMO + 1 energy = -2.80548 eV of complex **3**.

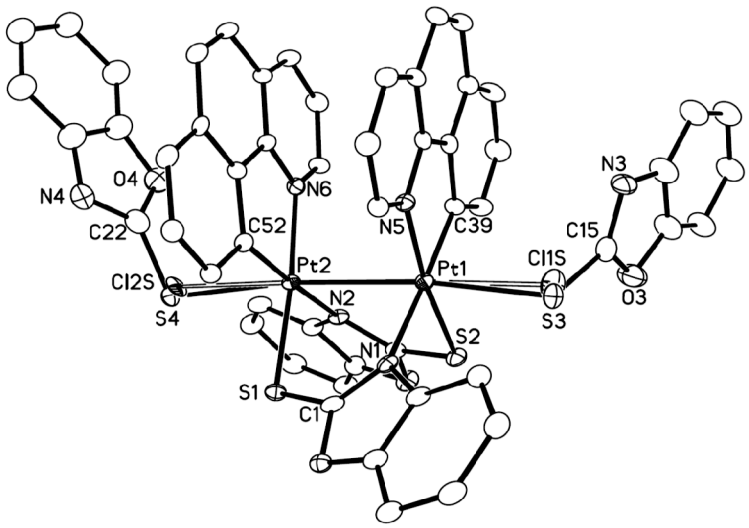


Figure 10. ORTEP diagram of complex **5** which is obtained by the recystallation of complex **4** in $CHCl_3$ and Et_2O (30% probability ellipsoids). Solvent molecules and hydrogen atoms are omitted. Selected bond lengths, distances (Å) and angles (°) : Pt(1)-Cl(1S) 2.37(3), Pt(2)-Cl(2S) 2.353(10), Pt(1)-S(3) 2.477(8), Pt(2)-S(4) 2.509(5), Pt(1)-C(39) 1.999(6), Pt(1)-N(5) 2.069(4), Pt(1)-N(1) 2.157(5), Pt(1)-S(2) 2.2977(14), Pt(1)-Pt(2) 2.6828(3), Pt(2)-C(52) 2.013(5), Pt(2)-N(6) 2.058(5), Pt(2)-N(2) 2.162(4), Pt(2)-S(1) 2.3103(14), C(39)-Pt(1)-N(5) 82.0(2), C(39)-Pt(1)-N(1) 176.4(2), N(5)-Pt(1)-N(1) 94.37(17), C(39)-Pt(1)-S(2) 93.18(17), N(5)-Pt(1)-S(2) 173.40(13), N(1)-Pt(1)-S(2) 90.47(12), C(39)-Pt(1)-Cl(1S) 82.2(5), N(5)-Pt(1)-Cl(1S) 92.0(8), N(1)-Pt(1)-Cl(1S) 98.2(5), S(2)-Pt(1)-Cl(1S) 82.9(7),C(39)-Pt(1)-S(3) 91.6(2), N(5)-Pt(1)-S(3) 89.7(2), N(1)-Pt(1)-S(3) 88.62(18), S(2)-Pt(1)-S(3) 85.92(19), Cl(1S)-Pt(1)-S(3) 10.1(5), C(52)-Pt(2)-N(6) 82.1(2), C(52)-Pt(2)-N(2) 177.3(2), N(6)-Pt(2)-N(2) 95.26(17), C(52)-Pt(2)-S(1) 94.70(16), N(6)-Pt(2)-S(1) 175.29(13), N(2)-Pt(2)-S(1) 87.99(13), C(52)-Pt(2)-Cl(2S) 85.3(14), N(6)-Pt(2)-Cl(2S) 89.1(12), N(2)-Pt(2)-Cl(2S) 95.1(14), S(1)-Pt(2)-Cl(2S) 87.3(12), C(52)-Pt(2)-S(4) 87.6(4), N(6)-Pt(2)-S(4) 93.6(3), N(2)-Pt(2)-S(4) 93.0(4)，S(1)-Pt(2)-S(4) 82.8(3), Cl(2S)-Pt(2)-S(4) 4.8(15).

[1] J. M. Soler, E. Artacho, J. D. Gale, A. García, J. Junquera, P. Ordejón and D. Sánchez-Portal, *J. Phys. Condens. Matter* 2002, **14**, 2745-2779.
[2] N. Troullier and J. L. Martins, *Phys. Rev. B* 1991, **43**, 1993-2006.
[3] J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.* 1996, **77**, 3865-3868.