Electronic Supplementary Material (ESI) for Dalton Transactions.


# Transition Metal Complex Directed Lead Bromides with Tunable Structures and Visible Light Driven Photocatalytic Properties

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**Table S1**. Selected bond lengths (Å) for compound **1**.

| | | | |
|---|---|---|---|
| Pb(1)-Br(8)#1 | 3.039(2) | Pb(3)-Br(7)#2 | 2.891(2) |
| Pb(1)-Br(8) | 3.039(2) | Pb(3)-Br(3) | 3.026(2) |
| Pb(1)-Br(8)#2 | 3.039(2) | Pb(3)-Br(5)#1 | 3.055(2) |
| Pb(1)-Br(5)#2 | 3.055(2) | Pb(3)-Br(4) | 3.092(2) |
| Pb(1)-Br(5)#1 | 3.055(2) | Pb(3)-Br(8) | 3.104(2) |
| Pb(1)-Br(5) | 3.055(2) | Pb(3)-Br(2) | 3.162(2) |
| Pb(2)-Br(6) | 2.823(2) | Co(1)-N(2) | 1.986(15) |
| Pb(2)-Br(1) | 2.869(2) | Co(1)-N(1) | 2.033(18) |
| Pb(2)-Br(4) | 2.903(2) | Co(1)-Br(3) | 2.394(3) |
| Pb(2)-Br(7) | 3.174(2) | Co(1)-Br(2) | 2.457(3) |
| Co(3)-N(6) | 2.051(11) | Co(2)-N(3)#1 | 2.068(15) |
| Co(3)-N(6)#1 | 2.051(11) | Co(2)-N(3)#2 | 2.068(15) |
| Co(3)-N(6)#2 | 2.051(11) | Co(2)-N(3) | 2.068(15) |
| Co(3)-N(5) | 2.155(15) | Co(2)-N(4) | 2.078(13) |
| Co(3)-N(5)#1 | 2.155(15) | Co(2)-N(4)#2 | 2.078(13) |
| Co(3)-N(5)#2 | 2.155(15) | Co(2)-N(4)#1 | 2.078(13) |

Symmetry transformations used to generate equivalent atoms: #1 -*y*+1, *x*-*y*, *z*; #2 -*x*+*y*+1, -*x*+1, *z*.

**Table S2**. Selected bond lengths (Å) for compound **2**.

| | | | |
|---|---|---|---|
| Pb(1)-Br(2) | 2.9504(8) | Co(1)-N(2) | 1.971(6) |
| Pb(1)-Br(1) | 2.9564(8) | Co(1)-N(3) | 1.982(5) |
| Pb(1)-Br(2)#1 | 3.0027(8) | Co(1)-N(1) | 2.073(6) |
| Pb(1)-Br(3) | 3.0441(8) | Co(1)-N(4) | 2.126(6) |
| Pb(1)-Br(3)#1 | 3.1097(8) | Co(1)-Br(4) | 2.4191(12) |
| Pb(1)-Br(1)#2 | 3.1330(9) | | |

Symmetry transformations used to generate equivalent atoms: #1 -*x*+3/2, *y*-1/2, *z*; #2 -*x*+3/2, *y*+1/2, *z*.

**Table S3**. Selected bond lengths (Å) for compound **3**.

| | | | |
|---|---|---|---|
| Pb(1)-Br(2) | 2.8082(13) | Pb(3)-Br(9) | 2.9661(10) |
| Pb(1)-Br(7) | 3.0031(12) | Pb(3)-Br(9)#1 | 2.9661(10) |
| Pb(1)-Br(8) | 3.0221(12) | Pb(3)-Br(10) | 2.9952(11) |
| Pb(1)-Br(10) | 3.0912(12) | Pb(3)-Br(10)#1 | 2.9952(11) |
| Pb(1)-Br(4) | 3.1072(12) | Pb(3)-Br(7)#1 | 3.0620(13) |
| Pb(2)-Br(12) | 2.9530(11) | Pb(3)-Br(7) | 3.0620(13) |
| Pb(2)-Br(4)#1 | 2.9635(12) | Pb(4)-Br(11)#2 | 2.899(12) |
| Pb(2)-Br(9) | 3.0005(11) | Pb(4)-Br(1) | 2.959(12) |
| Pb(2)-Br(3) | 3.0283(14) | Pb(4)-Br(5)#2 | 3.010(16) |
| Pb(2)-Br(11) | 3.0906(11) | Pb(4)-Br(11) | 3.079(12) |
| Pb(2)-Br(8)#1 | 3.0914(13) | Pb(4)-Br(5) | 3.086(15) |
| Co(1)-N(1) | 2.075(7) | Pb(4)-Br(1)#2 | 3.167(12) |
| Co(1)-N(4) | 2.080(7) | Pb(5)-Br(6) | 2.8825(12) |
| Co(1)-N(6) | 2.084(7) | Pb(5)-Br(12) | 3.0081(12) |
| Co(1)-N(3) | 2.089(7) | Pb(5)-Br(1) | 3.0475(15) |
| Co(1)-N(9) | 2.096(7) | Pb(5)-Br(5) | 3.0564(14) |
| Co(1)-N(5) | 2.099(7) | Pb(5)-Br(3) | 3.1222(14) |
| Co(2)-N(12) | 2.043(9) | Pb(5)-Br(11) | 3.2223(11) |
| Co(2)-N(2) | 2.097(7) | Co(2)-N(7) | 2.103(7) |
| Co(2)-N(8) | 2.098(8) | Co(2)-N(10) | 2.103(8) |
| | | Co(2)-N(11) | 2.109(9) |

Symmetry transformations used to generate equivalent atoms: #1 -*x*, -*y*+1, -*z*; #2 -*x*, -*y*+1, -*z*+1.

**Table S4**. Selected bond lengths (Å) for compound **4**.

| | | | |
|---|---|---|---|
| Pb(1)-Br(5) | 2.8081(11) | Pb(3)-Br(10) | 2.8662(11) |
| Pb(1)-Br(4) | 3.0019(11) | Pb(3)-Br(6) | 3.0079(10) |
| Pb(1)-Br(1) | 3.0844(10) | Pb(3)-Br(11) | 3.0782(12) |
| Pb(1)-Br(2) | 3.0930(11) | Pb(3)-Br(9) | 3.1246(11) |
| Pb(1)-Br(3) | 3.1679(10) | Pb(3)-Br(12) | 3.1356(11) |
| Pb(2)-Br(6) | 2.9541(9) | Pb(3)-Br(7) | 3.2258(10) |
| Pb(2)-Br(8) | 2.9891(10) | Pb(4)-Br(7)#1 | 2.9953(9) |
| Pb(2)-Br(3) | 3.0317(10) | Pb(4)-Br(7) | 2.9953(9) |
| Pb(2)-Br(7) | 3.1080(9) | Pb(4)-Br(11) | 3.0580(11) |
| Pb(2)-Br(9) | 3.1178(11) | Pb(4)-Br(11)#1 | 3.0580(11) |
| Pb(2)-Br(1) | 3.1209(11) | Pb(4)-Br(12)#1 | 3.1493(12) |
| Pb(5)-Br(8) | 2.9609(9) | Pb(4)-Br(12) | 3.1493(12) |
| Pb(5)-Br(8)#2 | 2.9609(9) | Pb(5)-Br(2)#2 | 2.9958(10) |
| Pb(5)-Br(2) | 2.9958(10) | Pb(5)-Br(4)#2 | 3.0662(12) |
| Ni-N(1) | 2.060(7) | Pb(5)-Br(4) | 3.0662(12) |
| Ni-N(4) | 2.090(6) | Ni(2)-N(12) | 2.084(6) |
| Ni-N(6) | 2.102(6) | Ni(2)-N(10) | 2.091(6) |
| Ni-N(5) | 2.100(6) | Ni(2)-N(7) | 2.095(7) |
| Ni-N(3) | 2.107(6) | Ni(2)-N(11) | 2.091(6) |
| Ni-N(2) | 2.124(7) | Ni(2)-N(8) | 2.097(6) |
| | | Ni(2)-N(9) | 2.101(6) |

Symmetry transformations used to generate equivalent atoms: #1 -*x*+1, -*y*+1, -*z*-1; #2 -*x*+1, -*y*+1, -*z*.

**Table S5**. Selected bond lengths (Å) for compound **5**.

| | | | |
|---|---|---|---|
| Pb(1)-Br(8) | 2.9247(18) | Pb(3)-Br(7) | 2.8332(19) |
| Pb(1)-Br(9) | 2.9589(18) | Pb(3)-Br(9)#1 | 3.0007(17) |
| Pb(1)-Br(4) | 3.040(2) | Pb(3)-Br(3) | 3.050(2) |
| Pb(1)-Br(6) | 3.0537(18) | Pb(3)-Br(8)#2 | 3.0701(18) |
| Pb(1)-Br(5) | 3.1414(19) | Pb(3)-Br(6) | 3.1393(18) |
| Pb(1)-Br(2) | 3.177(2) | Pb(3)-Br(4)#1 | 3.320(2) |
| Pb(2)-Br(2) | 2.862(2) | Co(1)-N(4) | 1.927(11) |
| Pb(2)-Br(1) | 2.888(2) | Co(1)-N(2) | 1.928(12) |
| Pb(2)-Br(5) | 3.0050(18) | Co(1)-N(1) | 1.937(11) |
| Pb(2)-Br(3) | 3.0739(19) | Co(1)-N(3) | 1.938(11) |
| Pb(2)-Br(6) | 3.0795(18) | Co(1)-N(6) | 1.939(11) |
| | | Co(1)-N(5) | 1.941(12) |

Symmetry transformations used to generate equivalent atoms: #1 *x*-1, *y*, *z*; #2 -*x*-1, -*y*, -*z*.

**Table S6**. Selected bond lengths (Å) for compound **6**.

| | | | |
|---|---|---|---|
| Pb(1)-Br(10) | 2.9128(8) | Pb(4)-Br(12) | 2.8500(8) |
| Pb(1)-Br(6) | 2.9847(8) | Pb(4)-Br(11) | 2.8912(8) |
| Pb(1)-Br(7) | 3.0195(8) | Pb(4)-Br(8) | 2.9728(8) |
| Pb(1)-Br(13) | 3.0231(8) | Pb(4)-Br(2)#1 | 3.1096(8) |
| Pb(1)-Br(9) | 3.0345(8) | Pb(5)-Br(4) | 2.7310(8) |
| Pb(1)-Br(5) | 3.2265(8) | Pb(5)-Br(6)#2 | 3.0218(8) |
| Pb(2)-Br(3) | 2.8709(9) | Pb(5)-Br(11) | 3.0663(8) |
| Pb(2)-Br(7) | 2.9021(8) | Pb(5)-Br(12) | 3.0886(8) |
| Pb(2)-Br(2) | 2.9948(8) | Pb(5)-Br(3)#3 | 3.1266(9) |
| Pb(2)-Br(6)#1 | 3.1599(8) | Co(1)-N(4) | 1.918(5) |
| Pb(2)-Br(13) | 3.1971(8) | Co(1)-N(1) | 1.922(5) |
| Pb(3)-Br(1) | 2.7215(10) | Co(1)-N(5) | 1.923(5) |
| Pb(3)-Br(8) | 2.9239(8) | Co(1)-N(3) | 1.925(5) |
| Pb(3)-Br(9)#1 | 2.9921(8) | Co(1)-N(2) | 1.933(5) |
| Pb(3)-Br(10) | 3.1735(8) | Co(1)-N(6) | 1.936(5) |

Symmetry transformations used to generate equivalent atoms: #1 *x*, -*y*+1/2, *z*+1/2; #2 -*x*+1, -*y*+1, -*z*+1; #3 -*x*+1, *y*+1/2, -*z*+3/2.

**Table S7**. The hydrogen bonds in compounds **1-6**.

| D-H···A | d(D-H) | d(H···A) | d(D···A) | <(DHA) |
|---|---|---|---|---|
| | | **1** | | |
| C(4)-H(4)···Br(1) | 0.93 | 3.014 | 3.652 | 127.15 |
| C(14)-H(14)···Br(4) | 0.93 | 2.837 | 3.587 | 138.57 |
| C(24)-H(24)···Br(4) | 0.93 | 2.758 | 3.493 | 136.88 |
| C(7)-H(7)···Br(6) | 0.93 | 2.850 | 3.583 | 136.70 |
| C(12)-H(12)···Br(7) | 0.93 | 2.781 | 3.563 | 142.39 |
| C(29)-H(29)···Br(7) | 0.93 | 2.906 | 3.683 | 141.96 |
| | | **2** | | |
| C(3)-H(3)···Br(2) | 0.93 | 2.90 | 3.7901 | 160 |
| C(10)-H(10)···Br(4) | 0.93 | 2.85 | 3.3446 | 114 |
| | | **3** | | |
| C(32)-H(32)···Br(6) | 0.93 | 2.86 | 3.7460 | 159 |
| C(47)-H(47)···Br(7) | 0.93 | 2.87 | 3.5815 | 135 |
| C(52)-H(52)···Br(10) | 0.93 | 2.72 | 3.5517 | 149 |
| C(65)-H(65)···Br(9) | 0.93 | 2.81 | 3.6733 | 154 |
| | | **4** | | |
| C(1) -H(1)···Br(4) | 0.93 | 2.82 | 3.5533 | 137 |
| C(26) -H(26)···Br(8) | 0.93 | 2.82 | 3.6687 | 153 |
| C(40) -H(40)···Br(2) | 0.93 | 2.73 | 3.5929 | 154 |
| C(43) -H(43)···Br(10) | 0.93 | 2.93 | 3.7900 | 154 |
| | | **5** | | |
| C(1) -H(1)···Br(3) | 0.93 | 2.90 | 3.6357 | 137 |
| C(13) -H(13)···Br(5) | 0.93 | 2.85 | 3.7183 | 156 |
| C(14) -H(14)···Br(8) | 0.93 | 2.90 | 3.6212 | 135 |
| C(23) -H(23)···Br(7) | 0.93 | 2.91 | 3.6341 | 135 |
| C(28) -H(28)···Br(3) | 0.93 | 2.66 | 3.5814 | 171 |
| C(30) -H(30)···Br(1) | 0.93 | 2.90 | 3.5405 | 127 |
| | | **6** | | |
| C(4) -H(4)···Br(13) | 0.93 | 2.81 | 3.4706 | 129 |
| C(12) -H(12)···Br(4) | 0.93 | 2.85 | 3.6962 | 151 |
| C(17) -H(17)···Br(12) | 0.93 | 2.90 | 3.6613 | 140 |
| C(28) -H(28)···Br(7) | 0.93 | 2.74 | 3.5688 | 149 |

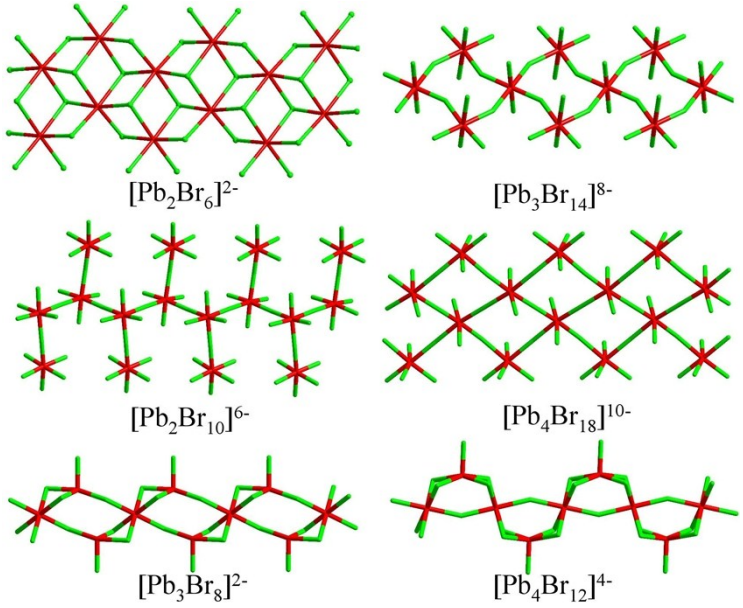


**Figure S1**. The variation of the partial structural motifs of the 1D Pb-Br chains directed by various organic cations.

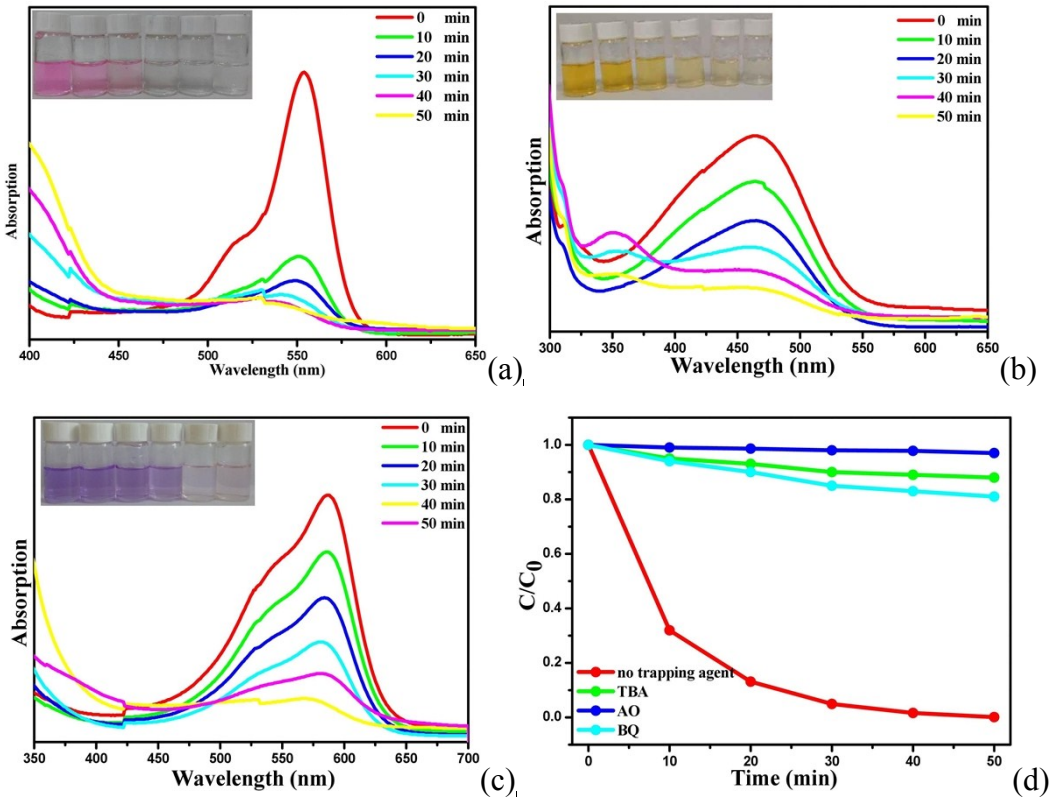


**Figure S2**. Absorption spectra of a solution of RhB (a), MO (b) and CV (c) in the presence of compound **6** under exposure to visible light irradiation. The time dependent photocatalytic degradation of CV under the radical-trapping scavengers over sample **6** (d).

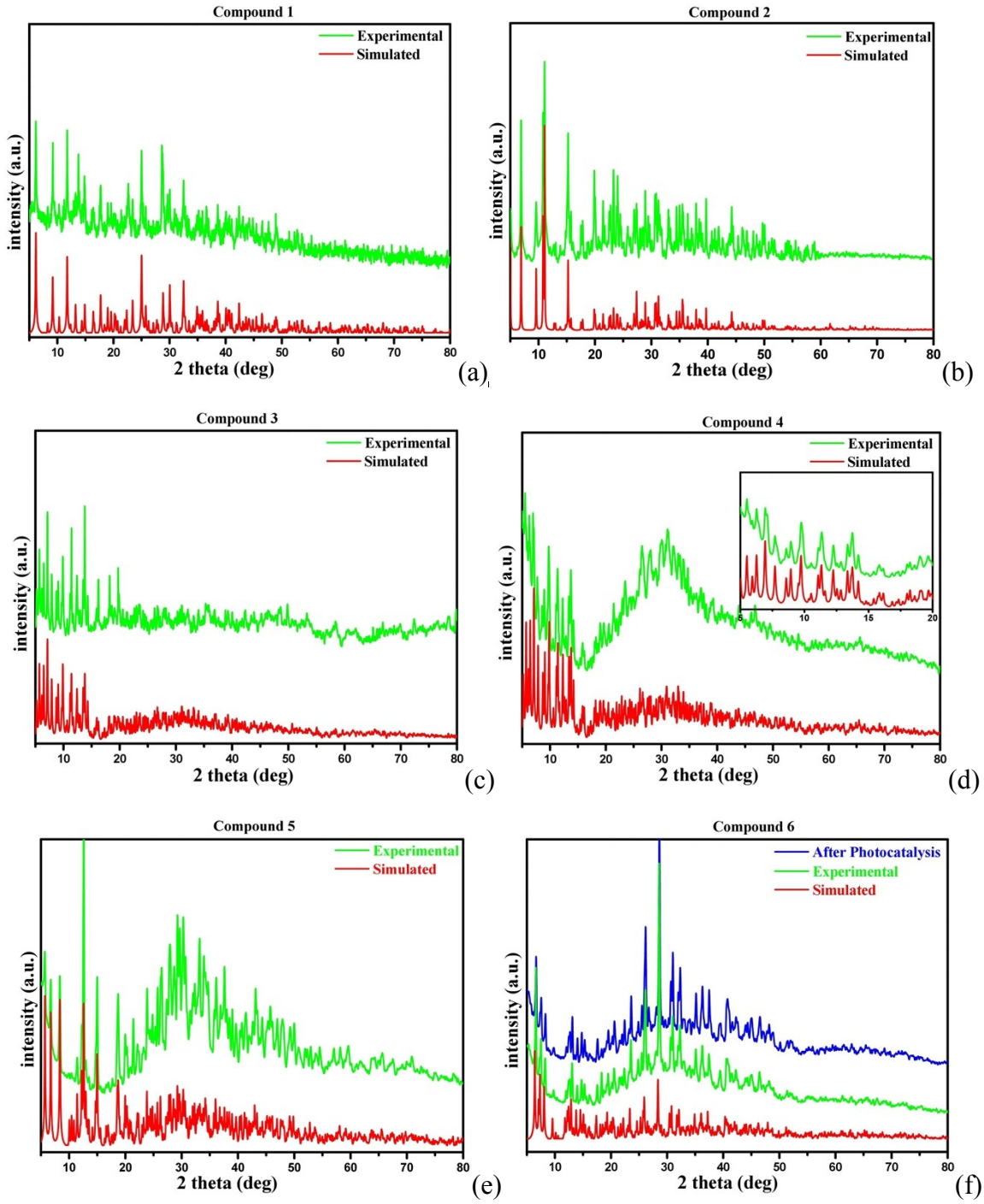


**Figure S3**. The simulated and experimental XRD patterns of compounds **1-6**.

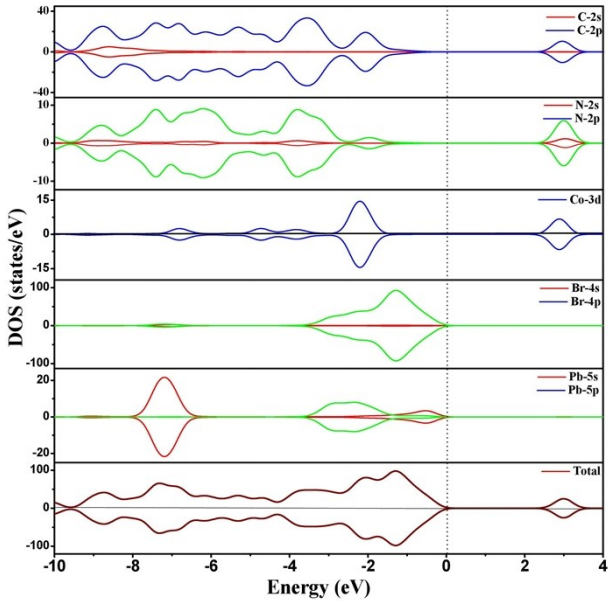


**Figure S4**. The total and partial DOS of compound **6**.