Supporting Information

Surface Morphology of Cu Adsorption on Different Terminations of the Hägg Iron Carbide (χ-Fe_5C_2) Phase

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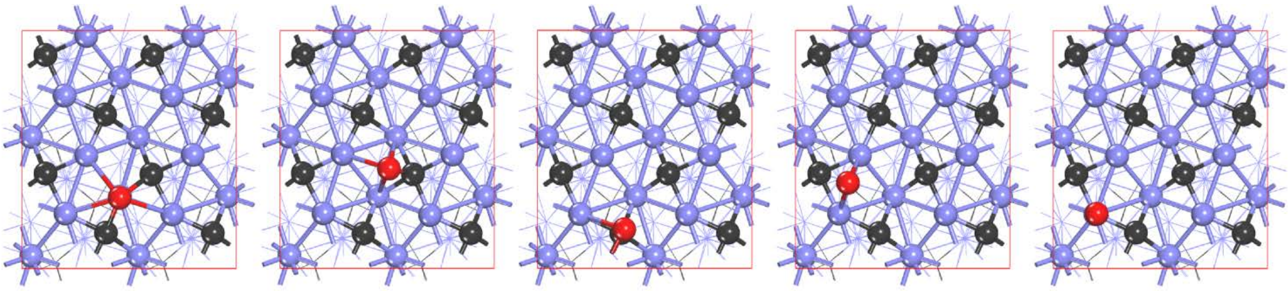
Table S1: Benchmark of slab thickness and relaxation thickness of single Cu atom adsorption on Fe_5C_2(100), Fe_5C_2(111), Fe_5C_2(510), Fe_5C_2(010) and Fe_5C_2(001) surfaces. (L represents total layers, R represents relaxed layers.)

Test	Fe_5C_2(100)		Fe_5C_2(111)		Fe_5C_2(510)	
		E_{ads}(eV)		E_{ads}(eV)		E_{ads}(eV)
Slab thickness	p(1×1)-4.60Å-7LR6	-2.82	p(2×1)-4.49Å-15LR12	-2.84	p(1×1)-5.18Å-8LR6	-3.27
	p(1×1)-5.72Å-8LR6	-2.82	p(2×1)-5.62Å-18LR12	-2.82	p(1×1)-5.63Å-9LR6	-3.26
	p(1×1)-7.06Å-10LR6	-2.86	p(2×1)-8.74Å-27LR12	-2.83	p(1×1)-7.22Å-11LR6	-3.30
	p(1×1)-9.02Å-12LR6	-2.80			p(1×1)-7.67Å-12LR6	-3.29
	p(1×1)-10.33Å-14LR6	-2.80			p(1×1)-9.71Å-15LR6	-3.29
Relaxation thickness	p(2×2)-5.72Å-8LR6	-2.84	p(2×1)-4.49Å-15LR11	-2.91	p(1×1)-5.63Å-9LR5	-3.26
	p(2×2)-5.72Å-8LR7	-2.82	p(2×1)-4.49Å-15LR12	-2.84	p(1×1)-5.63Å-9LR6	-3.26
	p(2×2)-5.72Å-8LR8	-2.85	p(2×1)-4.49Å-15LR13	-2.80	p(1×1)-5.63Å-9LR7	-3.26
			p(2×1)-4.49Å-15LR14	-2.79	p(1×1)-5.63Å-9LR8	-3.28

Test	Fe_5C_2(010)		Fe_5C_2(001)	
		E_{ads}(eV)		E_{ads}(eV)
Slab thickness	p(1×1)-4.04-8LR8	-3.31	p(1×1)-4.15Å-10LR8	-2.96
	p(1×1)-4.50-9LR8	-3.28	p(1×1)-6.07Å-14LR8	-2.93
	p(1×1)-5.07-10LR8	-3.28	p(1×1)-6.62Å-15LR8	-2.95
	p(1×1)-5.59-11LR8	-3.27	p(1×1)-9.09Å-20LR8	-2.93
	p(1×1)-6.74-13LR8	-3.26		
Relaxation thickness	p(1×1)-5.59-11LR6	-3.29	p(1×1)-6.07Å-14LR8	-2.93
	p(1×1)-5.59-11LR7	-3.29	p(1×1)-6.07Å-14LR9	-2.93
	p(1×1)-5.59-11LR8	-3.27	p(1×1)-6.07Å-14LR10	-2.92
	p(1×1)-5.59-11LR9	-3.25	p(1×1)-6.07Å-14LR11	-2.92
	p(1×1)-5.59-11LR10	-3.25	p(1×1)-6.07Å-14LR12	-2.92

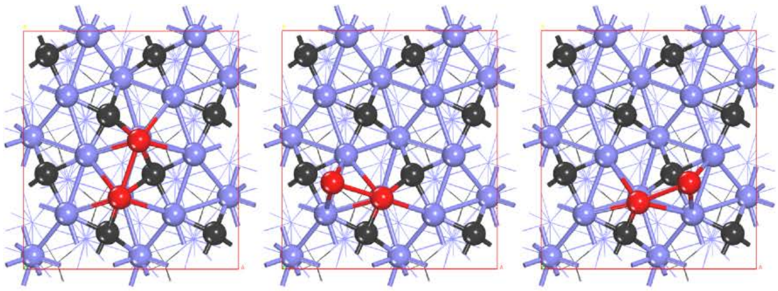
Figure S1. Various optimized $Cu_{1\text{-}13}$, Cu_{16} configurations on the $p(2\times2)$ $Fe_5C_2(100)$ surface (adsorption energy in eV)

Cu1

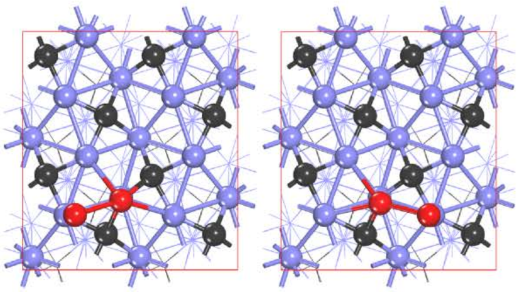


6F (–2.84) 4F (–2.57) 3F (–2.40) 2F (–2.18) 1F (–1.83)

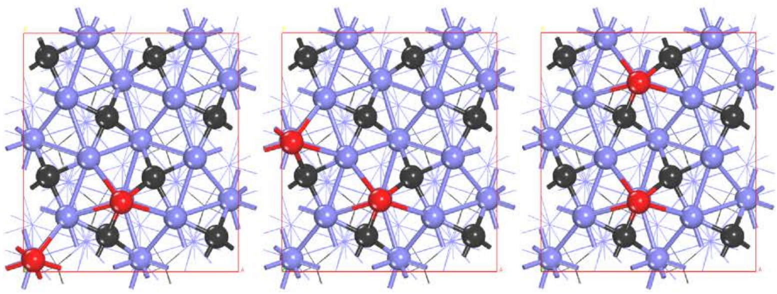
Cu2



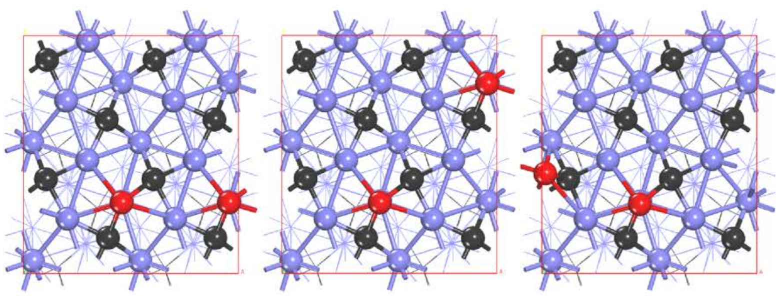
a1 (–6.00) a2 (–5.47) a3 (–5.44)



a4 (–5.23) a5 (–5.32)

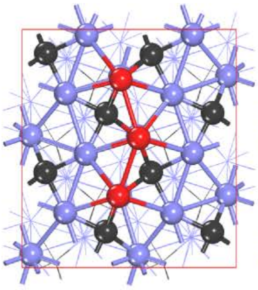


d1 (–5.69) d2 (–5.69) d3 (–5.68)



d4 (–5.66) d5 (–5.65) d6 (–5.44)

Cu3



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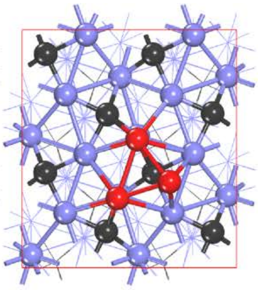
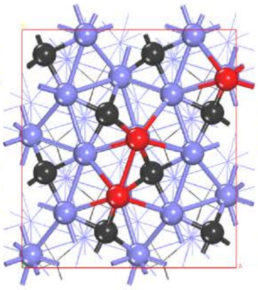
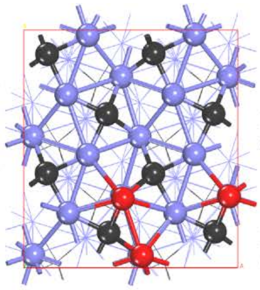


a2 (–8.92)



a3 (–8.83)



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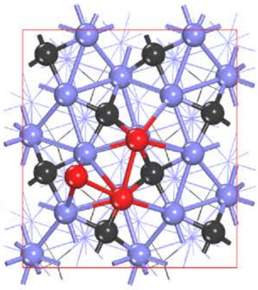
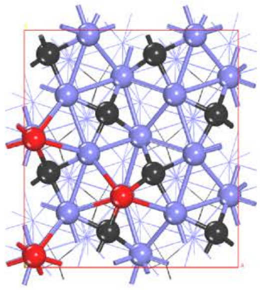
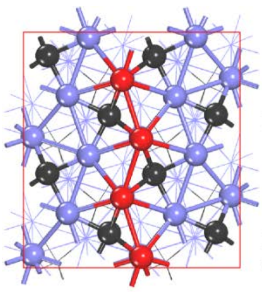


a5 (–8.68)



d1 (–8.52)

Cu4



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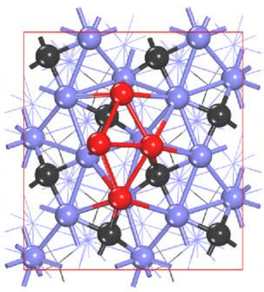

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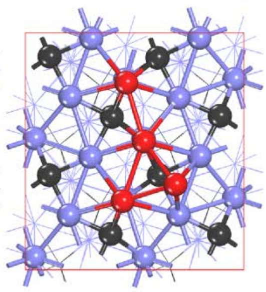

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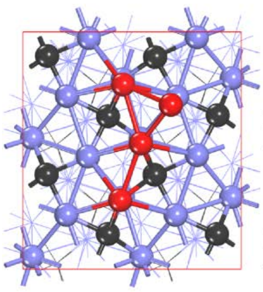
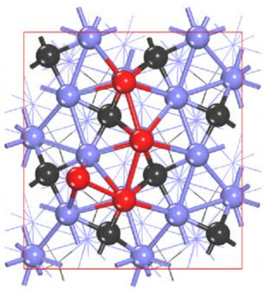


a4 (–12.01)



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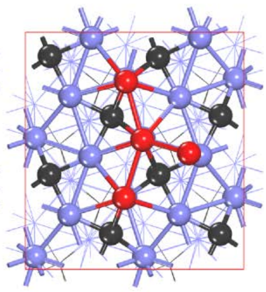
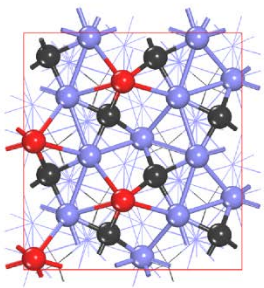
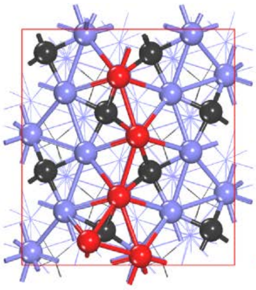


a6 (–11.55)



d1 (–11.35)

Cu5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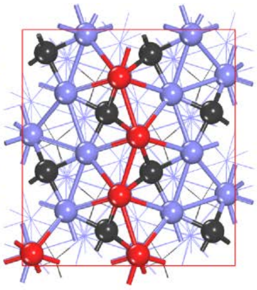
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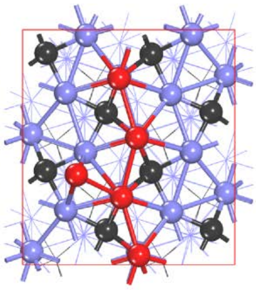
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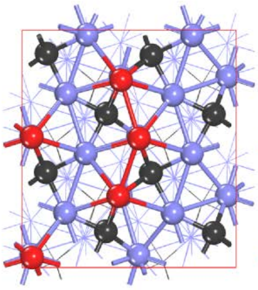
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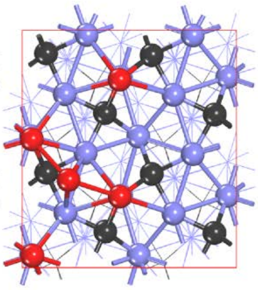
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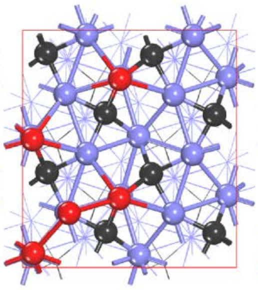
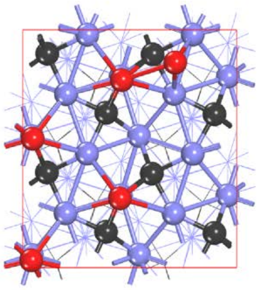
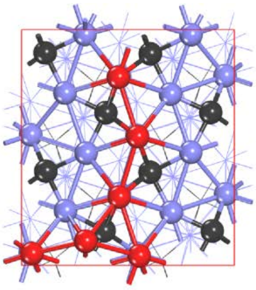

d3 (–14.20)


d4 (–14.05)

Cu6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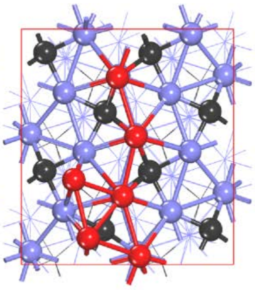
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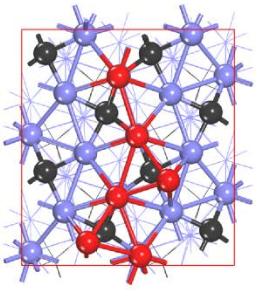
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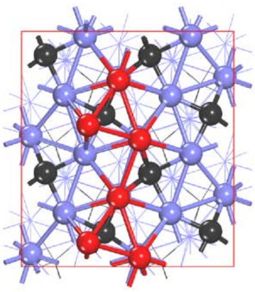
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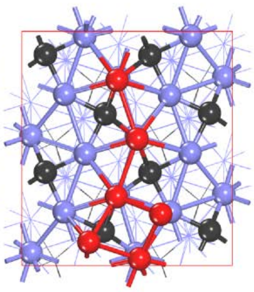
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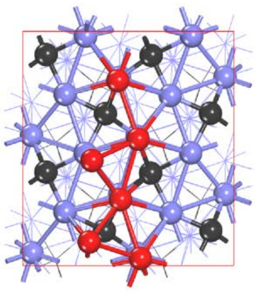
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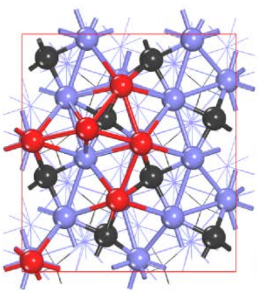
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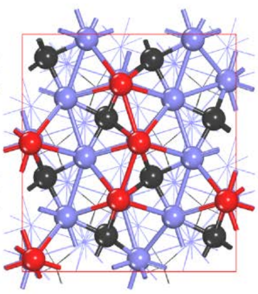
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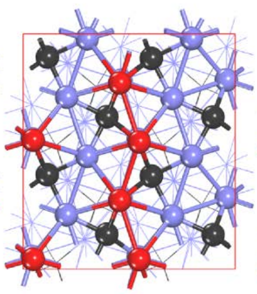
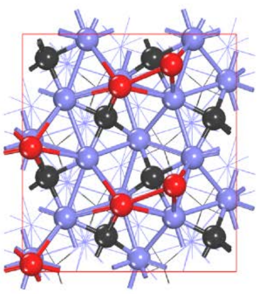

d3 (–18.11)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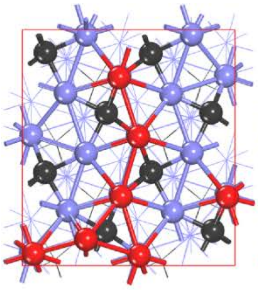
Cu7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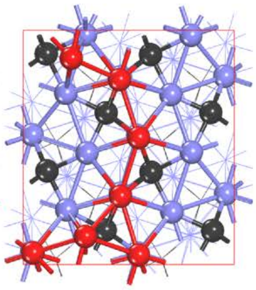
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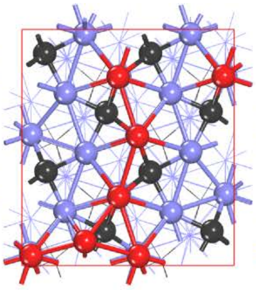
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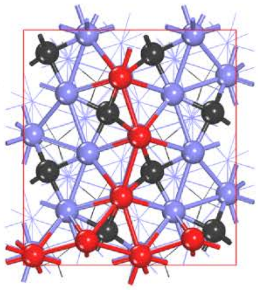
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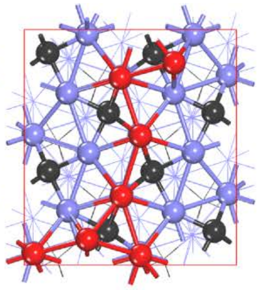
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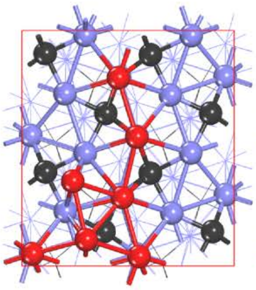
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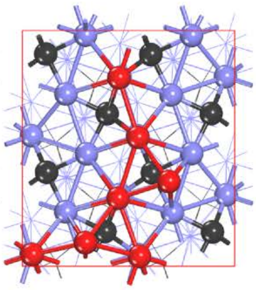
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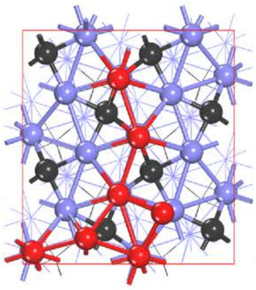
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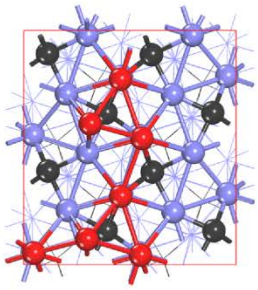
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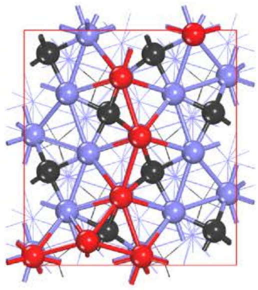
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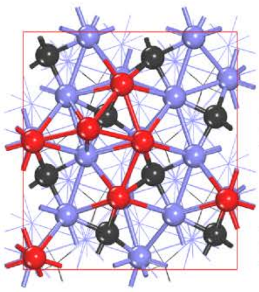
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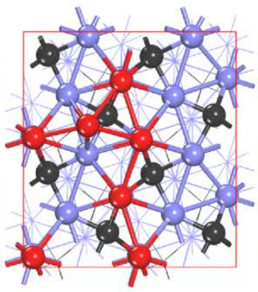
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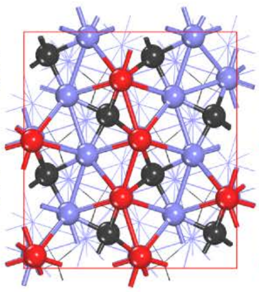
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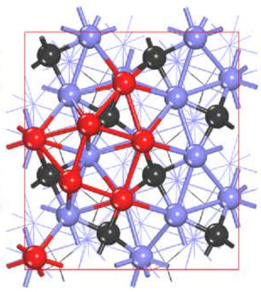
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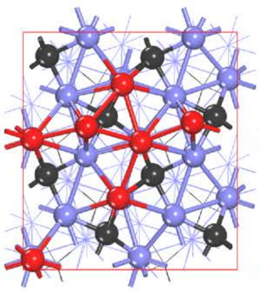
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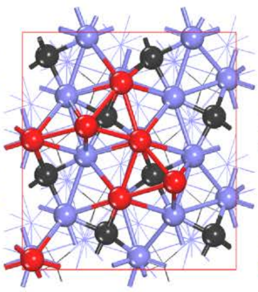
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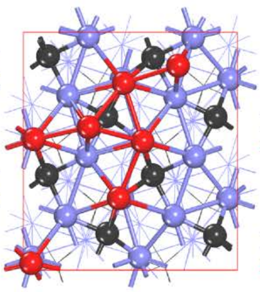
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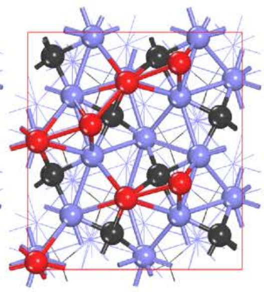
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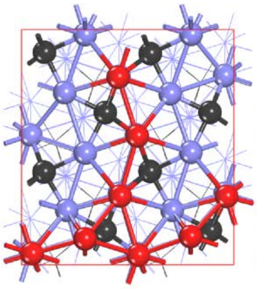
Cu8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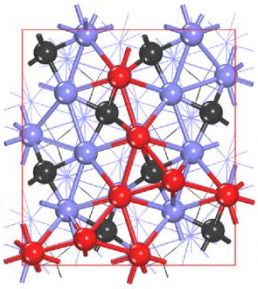
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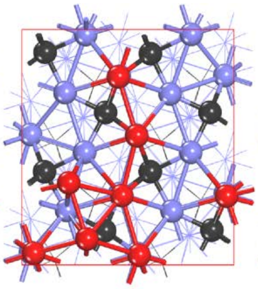
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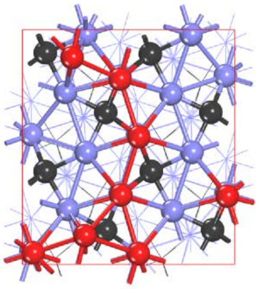
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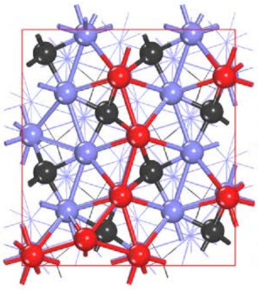
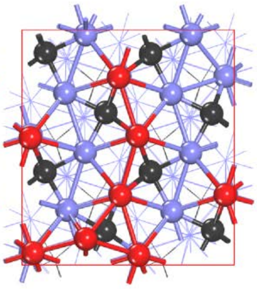
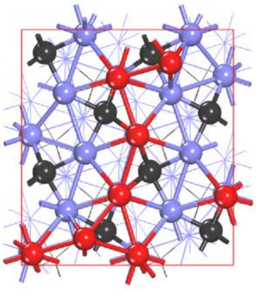
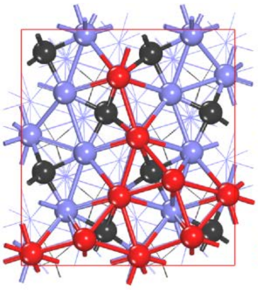
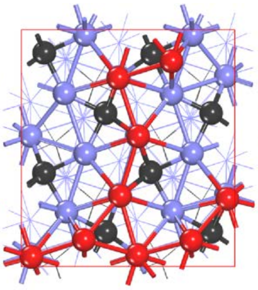

a5 (–24.94)

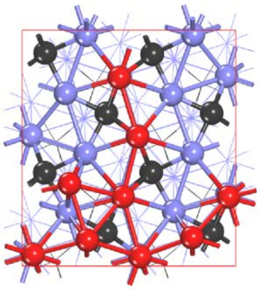

a6 (–24.92)

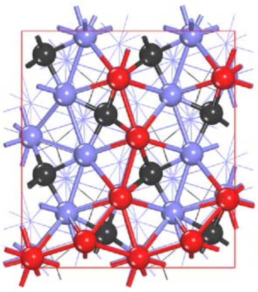

a7 (–24.87)

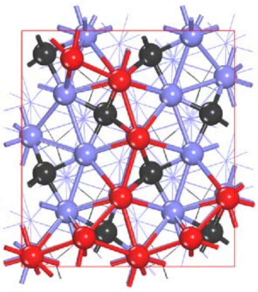
Cu9

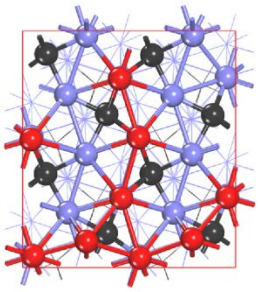

a1 (–28.75)


a2 (–28.52)

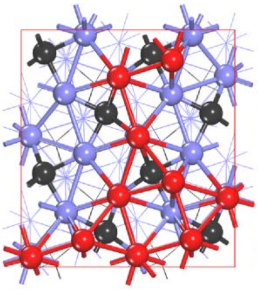

a3 (–28.42)


a4 (–28.40)

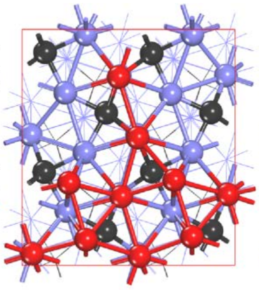

a5 (–28.34)


a6 (–28.28)

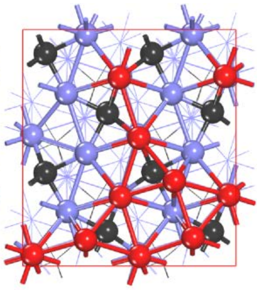
Cu10



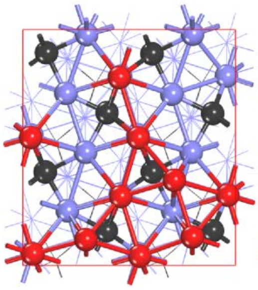
a1 (–32.02)



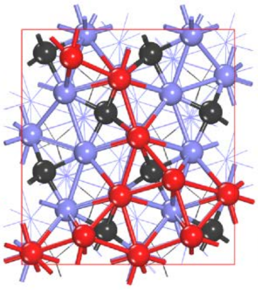
a2 (–31.92)



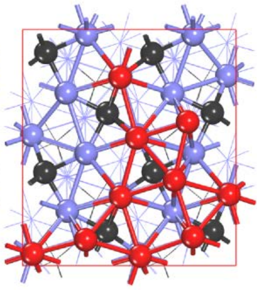
a3 (–31.88)



a4 (–31.84)

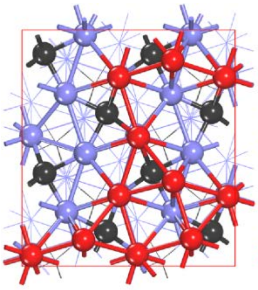


a5 (–31.82)

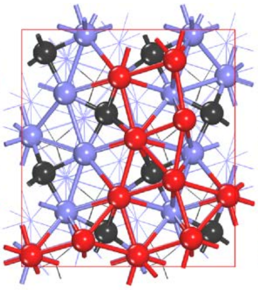


a6 (–31.75)

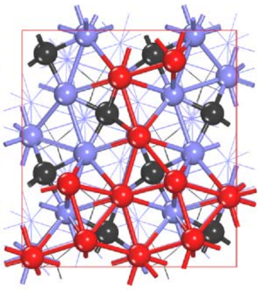
Cu11



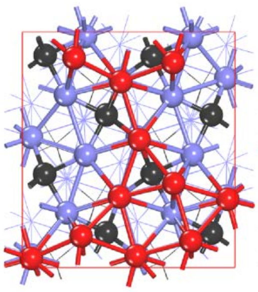
a1 (–35.42)



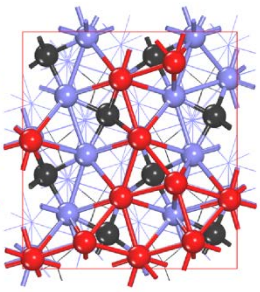
a2 (–35.29)



a3 (–35.17)

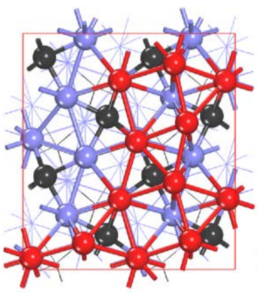


a4 (–35.11)

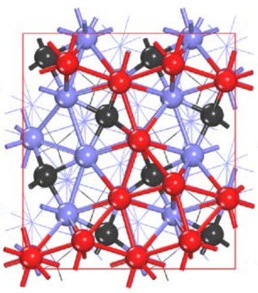


a5 (–35.08)

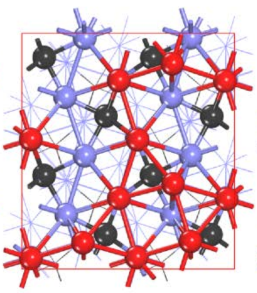
Cu12



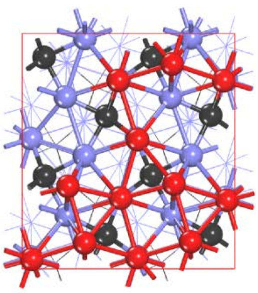
a1 (–38.88)



a2 (–38.86)

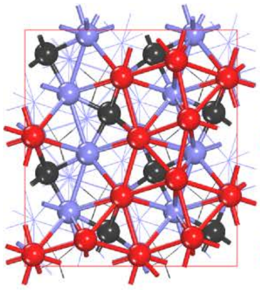


a3 (–38.75)

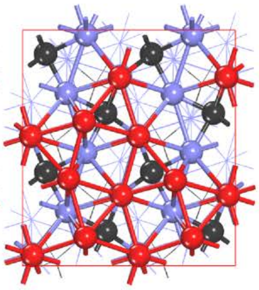


a4 (–38.60)

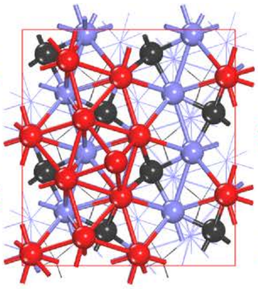
Cu13



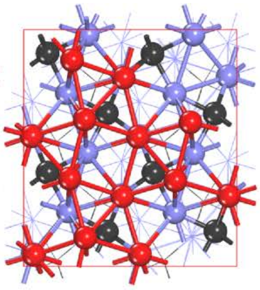
a1 (–42.55)



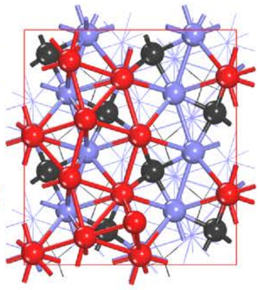
a2 (–42.28)



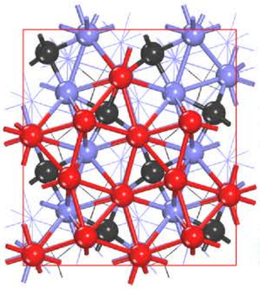
a3 (–42.19)



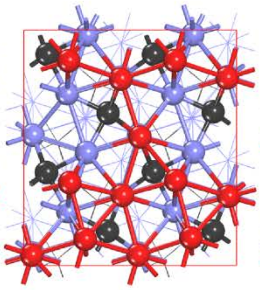
a4 (–42.09)



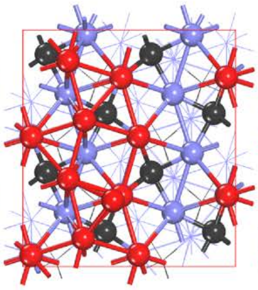
a5 (–42.08)



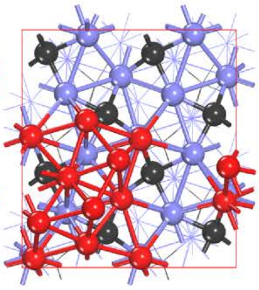
a6 (–42.07)



a7 (–42.06)

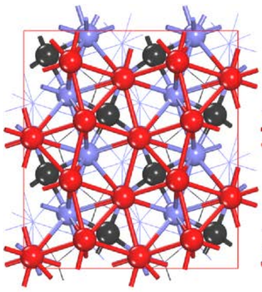


a8 (–41.95)

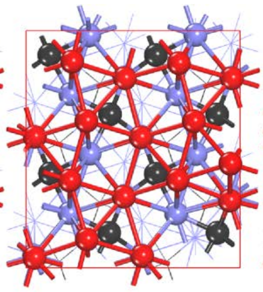


a9 (–40.28)

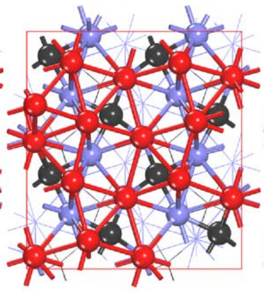
Cu16



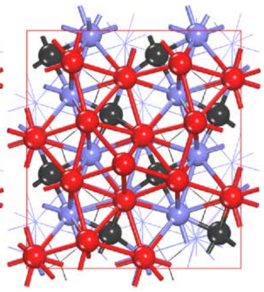
a1 (–53.23)



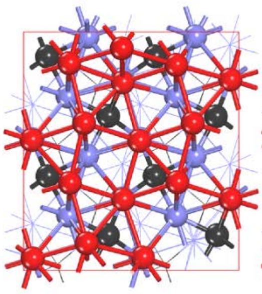
a2 (–52.75)



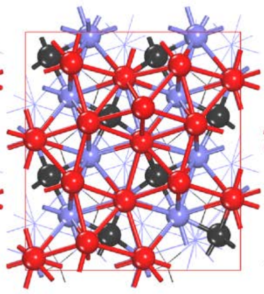
a3 (–52.74)



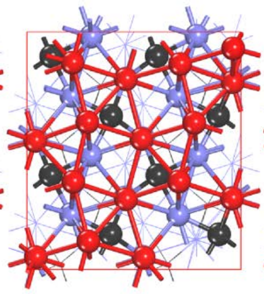
a4 (–52.73)



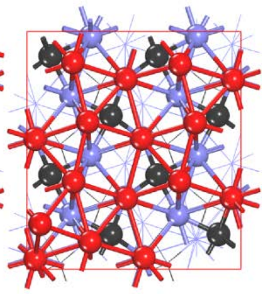
a5 (–52.73)



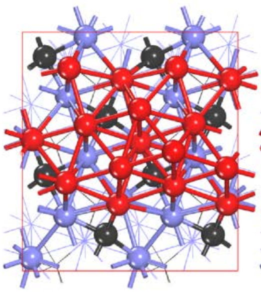
a6 (–52.71)



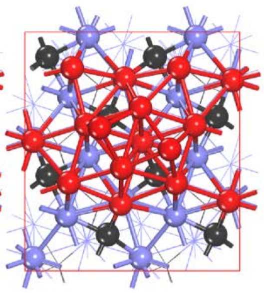
a7 (–52.53)



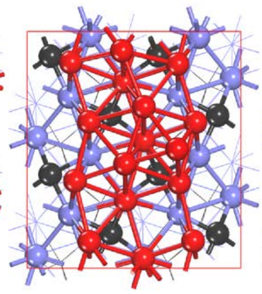
a8 (–52.47)



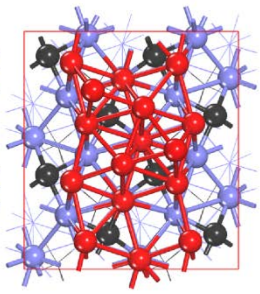
a9 (–51.71)



a10 (–50.81)



a11 (–50.05)



a12 (–49.37)

Figure S2. Diffusion pathways of single Cu atom on the Fe_5C_2(100) surface

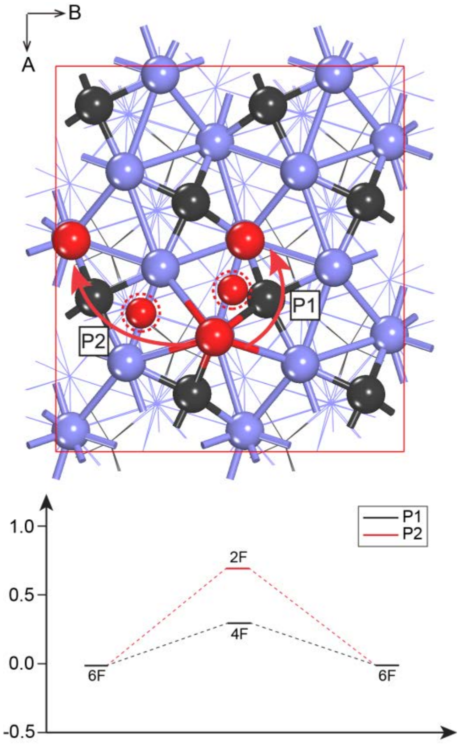
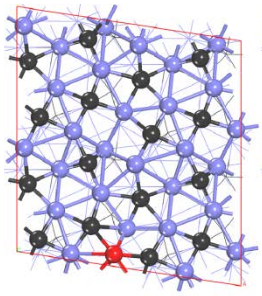
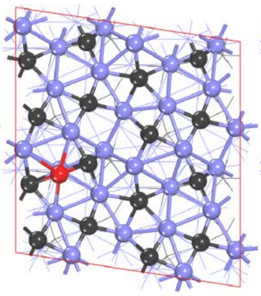


Figure S3. Various optimized $Cu_{1\text{-}14}$, Cu_{16} configurations on the p(2×2) Fe_5C_2(111) surface (adsorption energy in eV)

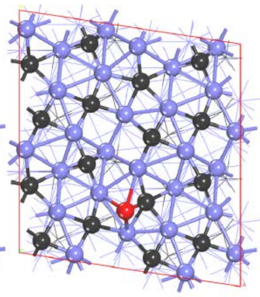
Cu1



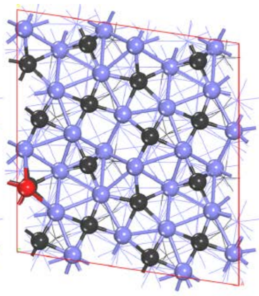
7F (–3.23)



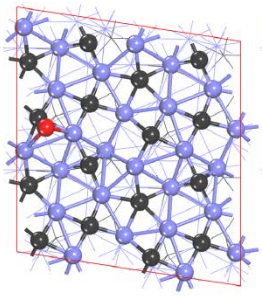
6F (–2.84)



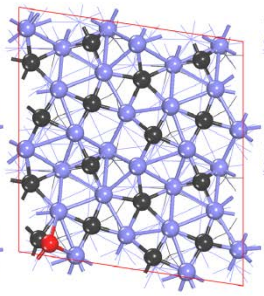
4F1 (–2.43)



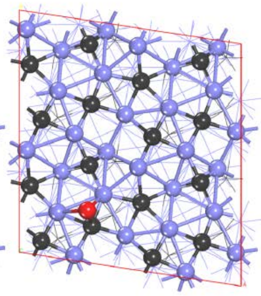
5F (–2.34)



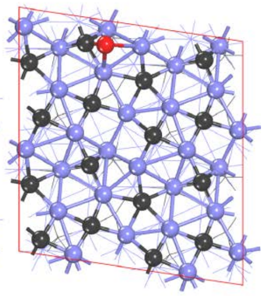
3F1 (–2.25)



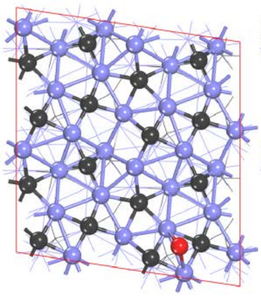
4F2 (–2.23)



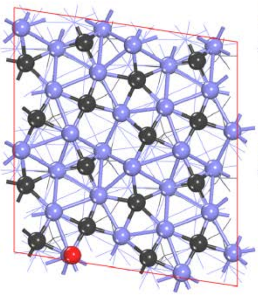
3F2 (–2.17)



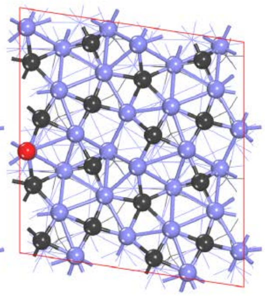
3F3 (–1.90)



2F (–1.90)

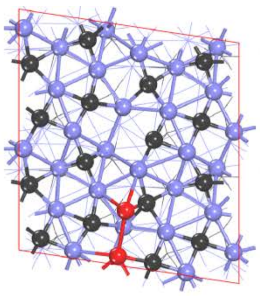


1F1 (–1.65)

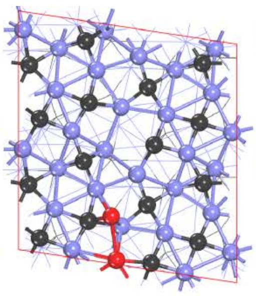


1F2 (–1.49)

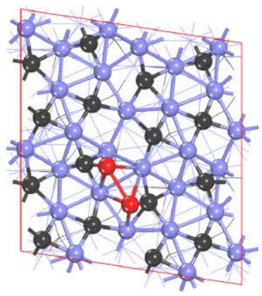
Cu2



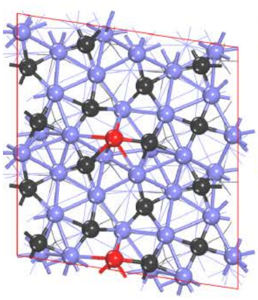
a1 (–6.01)



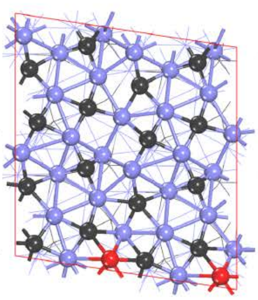
a2 (–5.95)



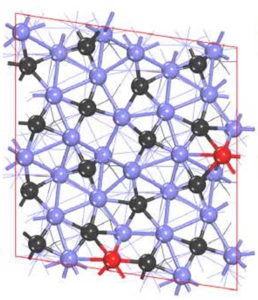
a3 (–5.62)



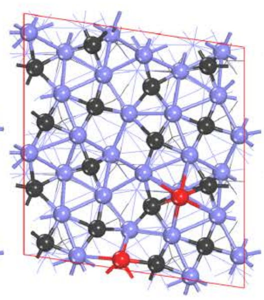
d1 (–6.78)



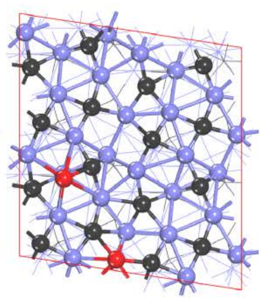
d2 (–6.40)



d3 (–6.36)

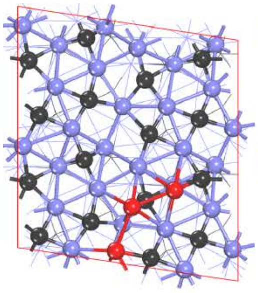


d4 (–6.16)

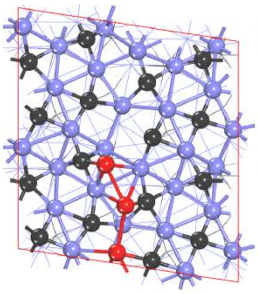


d5 (–6.05)

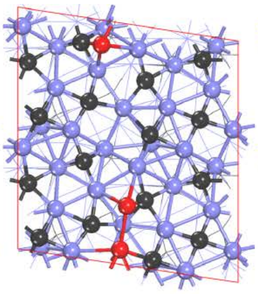
Cu3



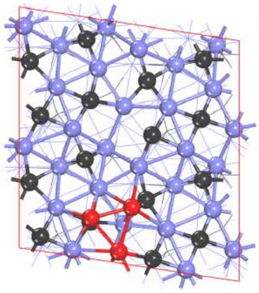
a1 (–9.36)



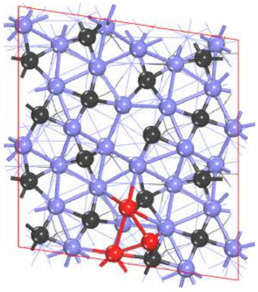
a2 (–9.23)



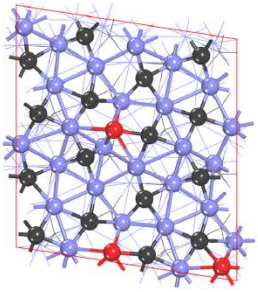
a3 (–8.96)



a4 (–8.87)

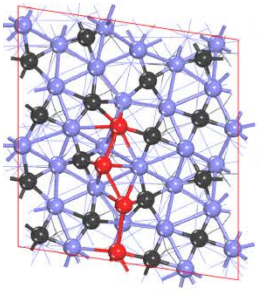


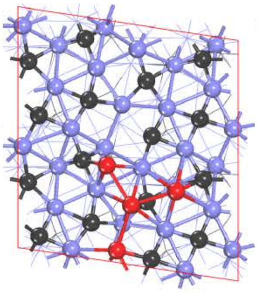
a5 (–8.78)

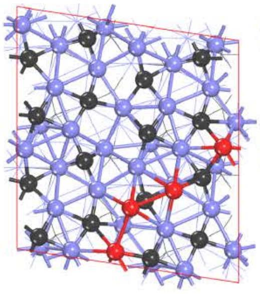


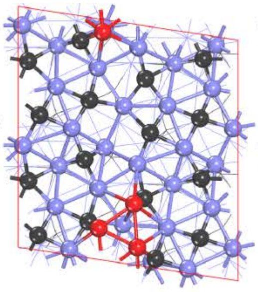
d1 (–9.77)

Cu4


a1 (–12.89)


a2 (–12.57)


a3 (–12.57)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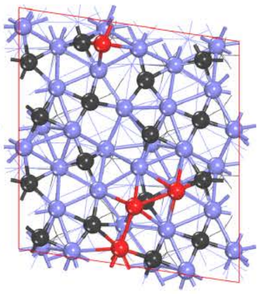
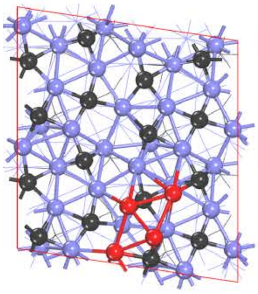
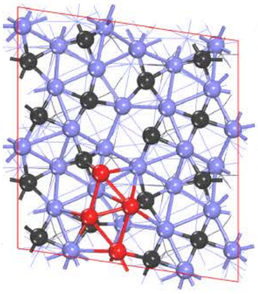
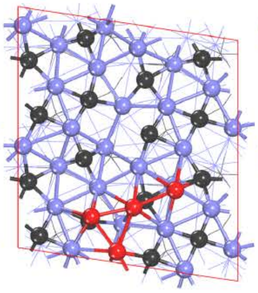
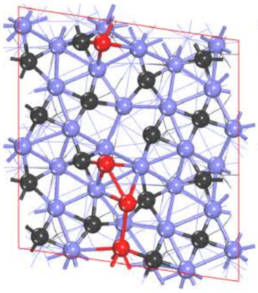
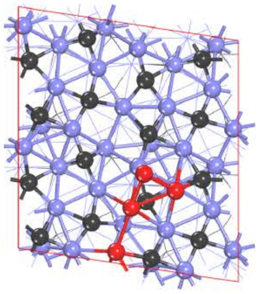

a5 (–12.34)

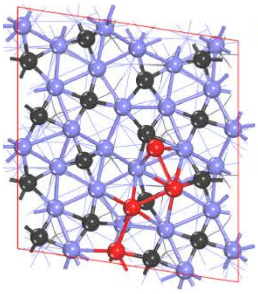

a6 (–12.33)

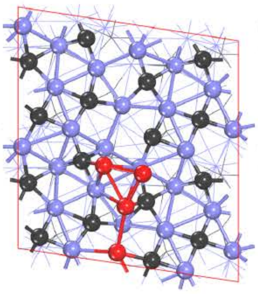

a7 (–12.33)

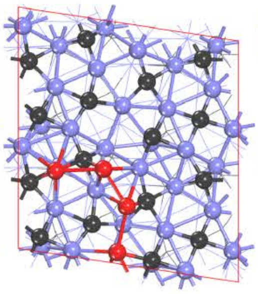

a8 (–12.26)

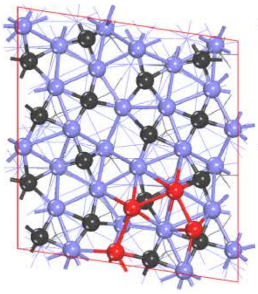

a9 (–12.21)

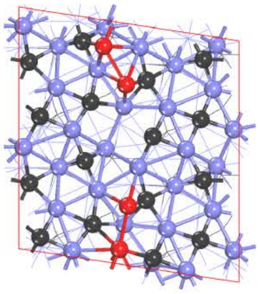

a10 (–12.20)

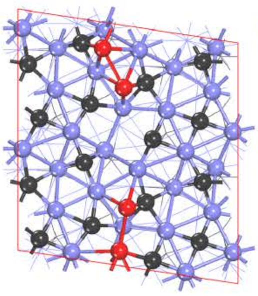

a11 (–12.13)

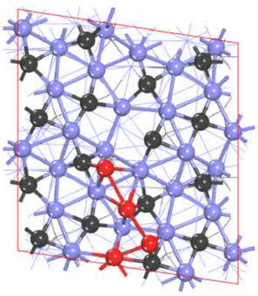

a12 (–12.11)

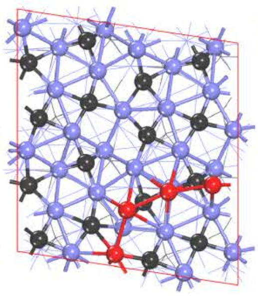

a13 (–12.08)

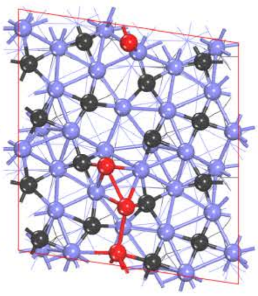

a14 (–11.98)

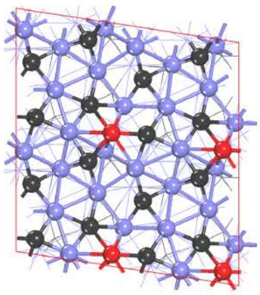

a15 (–11.97)


a16 (–11.96)

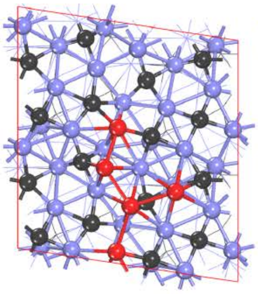

a17 (–11.96)


a18 (–11.72)

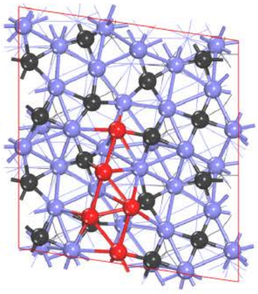

a19 (–11.29)


d1 (–12.91)

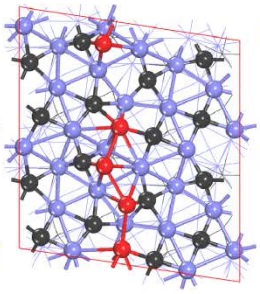
Cu5



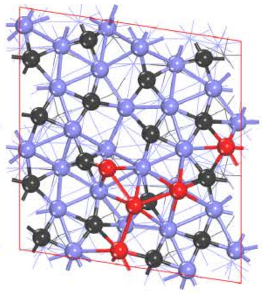
a1 (–16.18)



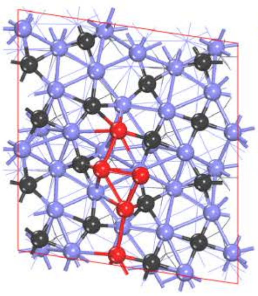
a2 (–15.95)



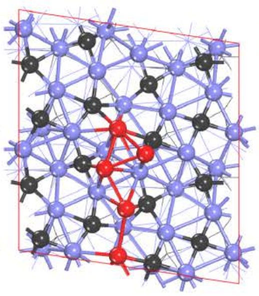
a3 (–15.80)



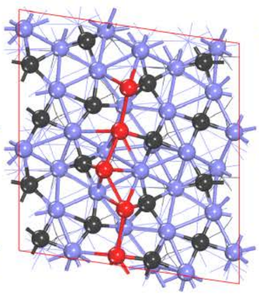
a4 (–15.72)



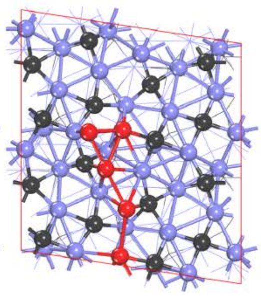
a5 (–15.71)



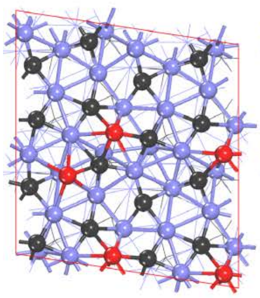
a6 (–15.71)



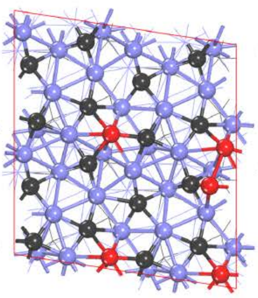
a7 (–15.57)



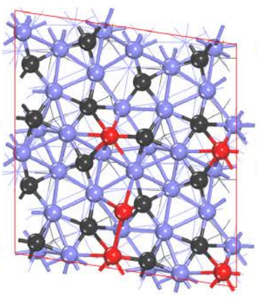
a8 (–15.51)



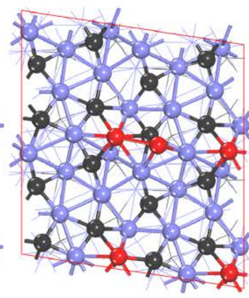
d1 (–16.09)



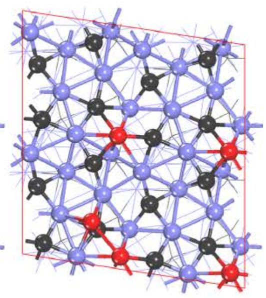
d2 (–15.78)



d3 (–15.59)

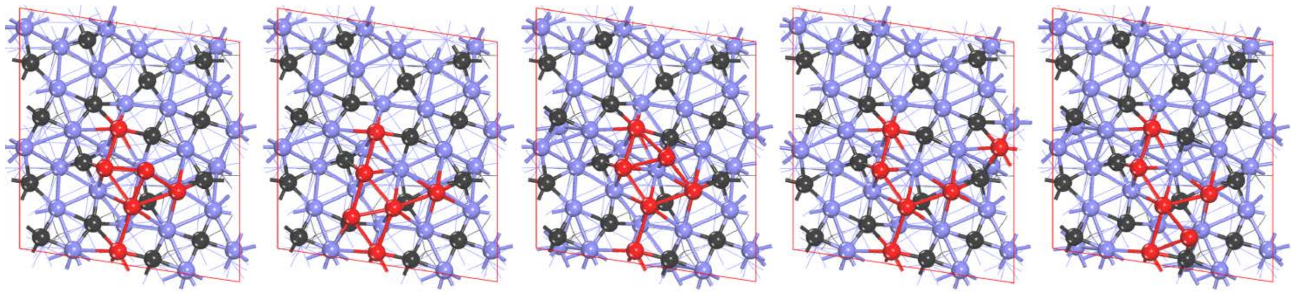


d4 (–15.36)

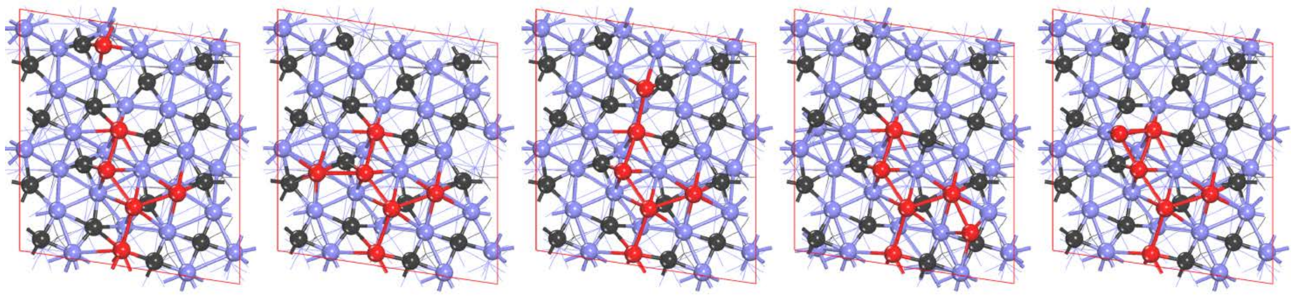


d5 (–15.33)

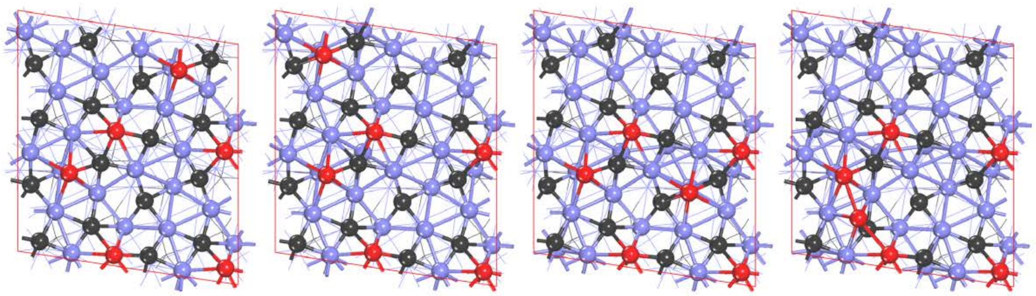
Cu6



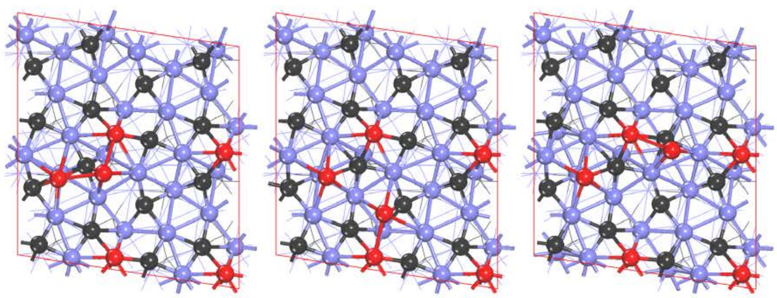
a1 (−19.35) a2 (−19.34) a3 (−19.34) a4 (−19.32) a5 (−19.13)



a6 (−19.13) a7 (−19.06) a8 (−18.88) a9 (−18.79) a10 (−18.78)

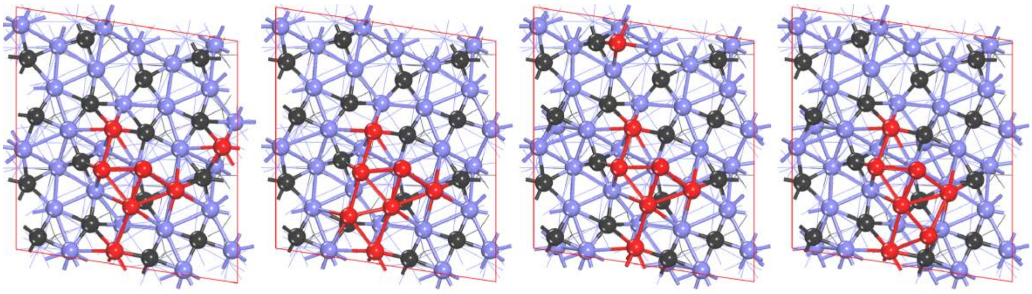


d1 (−19.26) d2 (−19.18) d3 (−19.17) d4 (−18.94)

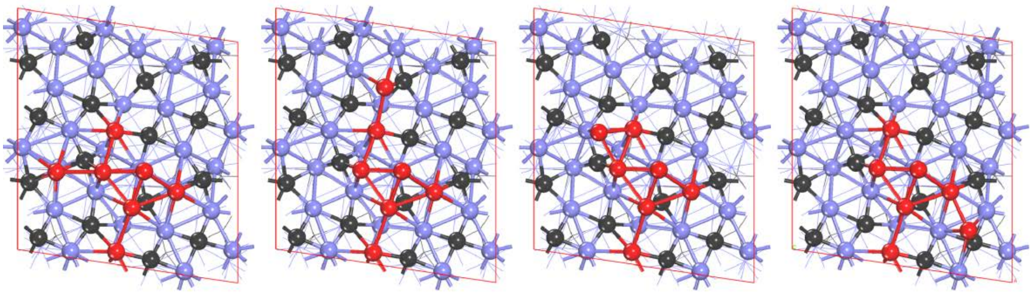


d5 (−18.72) d6 (−18.71) d7 (−18.41)

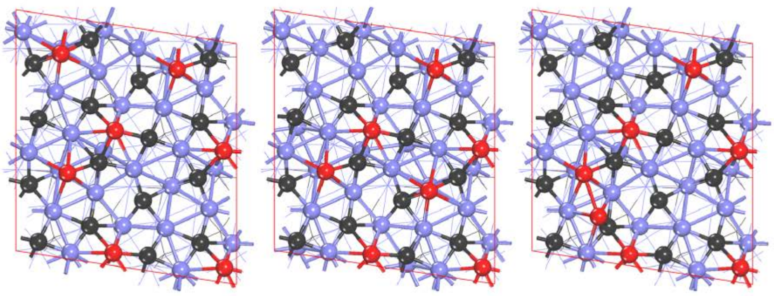
Cu7



a1 (–22.50) a2 (–22.49) a3 (–22.31) a4 (–22.26)

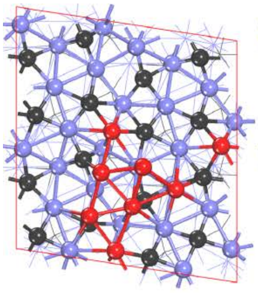


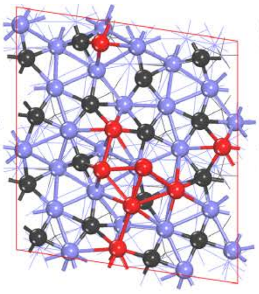
a5 (–22.23) a6 (–22.05) a7 (–21.96) a8 (–21.95)

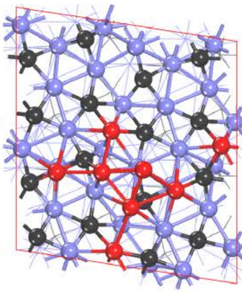


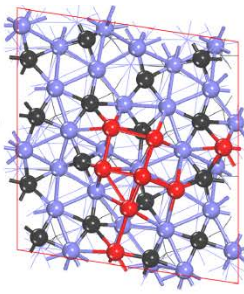
d1 (–22.34) d2 (–22.34) d3 (–22.11)

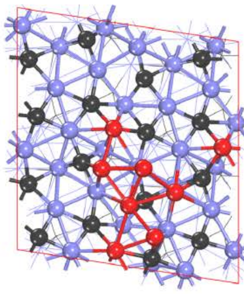
Cu8

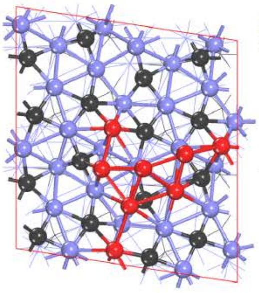

a1 (–25.69)

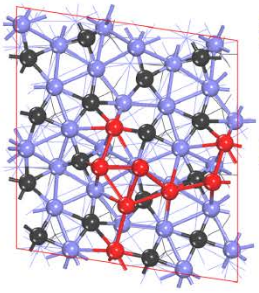

a2 (–25.47)

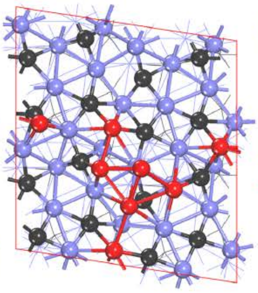

a3 (–25.46)

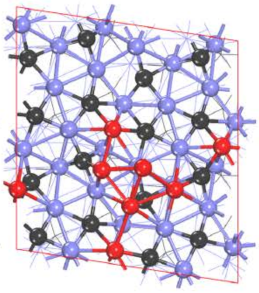

a4 (–25.44)

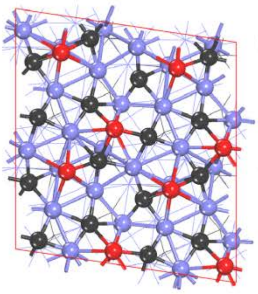

a5 (–25.42)

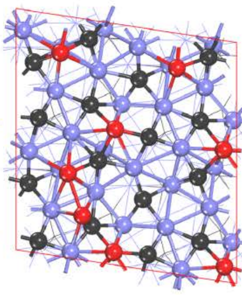

a6 (–25.19)

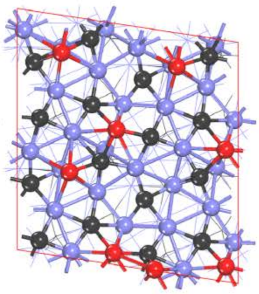

a7 (–25.17)


a8 (–24.92)

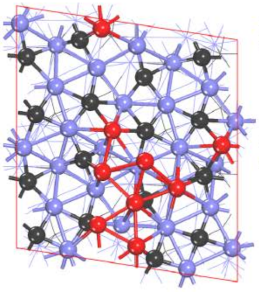

a9 (–24.80)

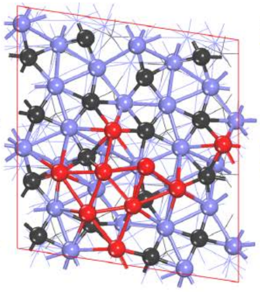

d1 (–25.40)

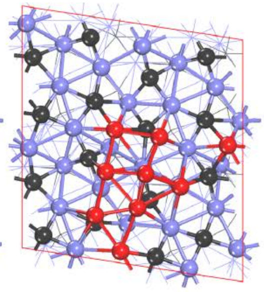

d2 (–25.19)

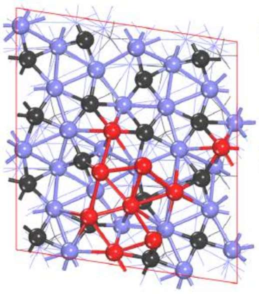

d3 (–25.13)

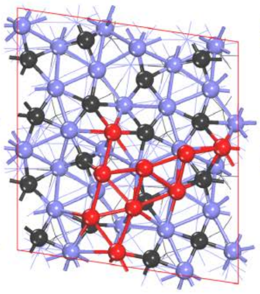
Cu9

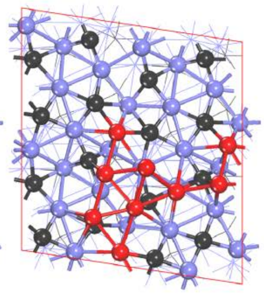

a1 (–29.10)

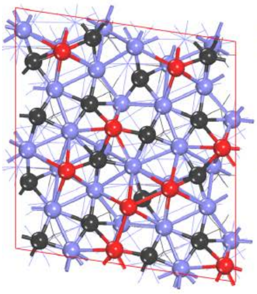

a2 (–28.98)

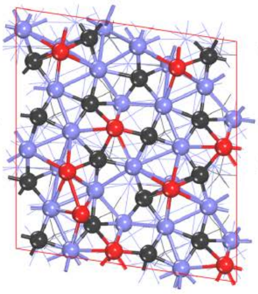

a3 (–28.67)

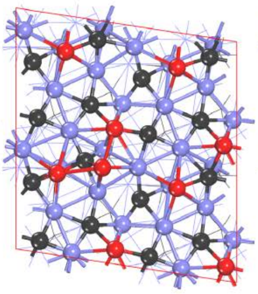

a4 (–28.62)

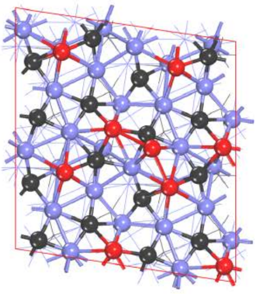

a5 (–28.38)


a6 (–28.26)

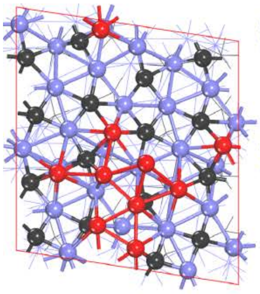

d1 (–28.43)


d2 (–28.26)

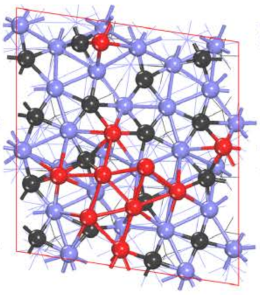

d3 (–28.21)


d4 (–28.16)

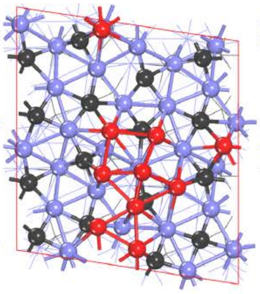
Cu10



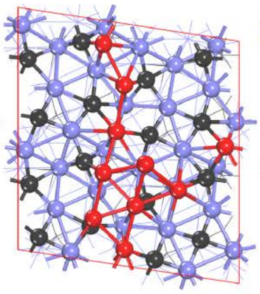
a1 (–32.20)



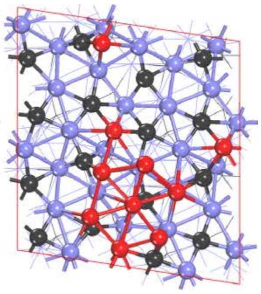
a2 (–32.05)



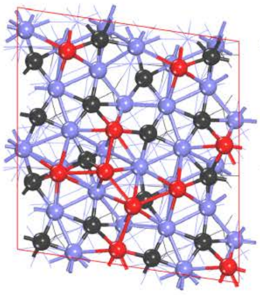
a3 (–31.96)



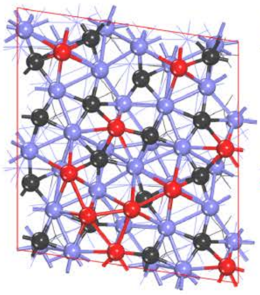
a4 (–31.95)



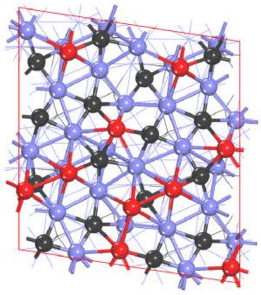
a5 (–31.66)



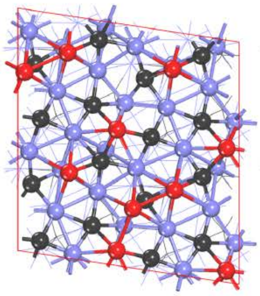
d1 (–31.77)



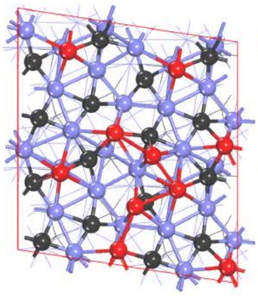
d2 (–31.58)



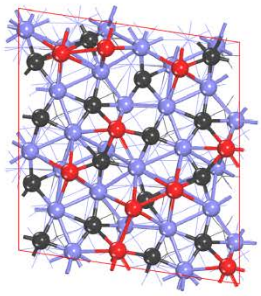
d3 (–31.56)



d4 (–31.45)

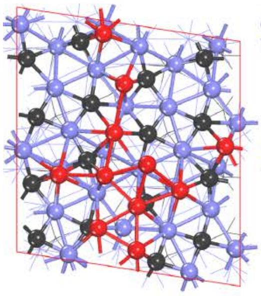


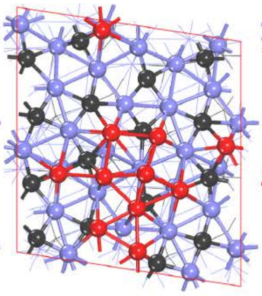
d5 (–31.41)

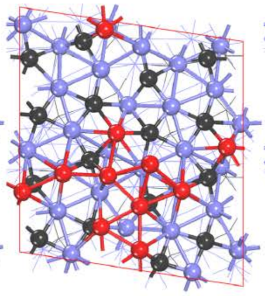


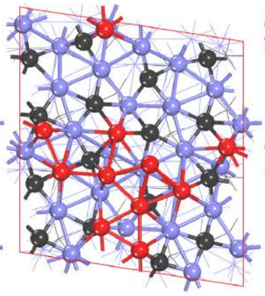
d6 (–31.21)

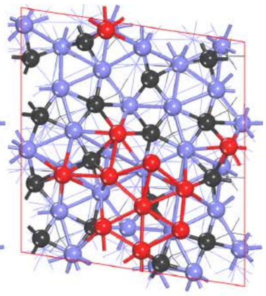
Cu11

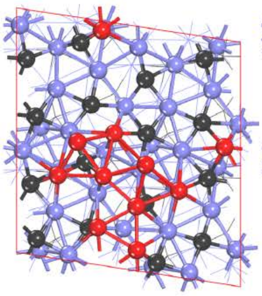

a1 (–35.09)


a2 (–35.06)


a3 (–35.00)


a4 (–34.98)


a5 (–34.94)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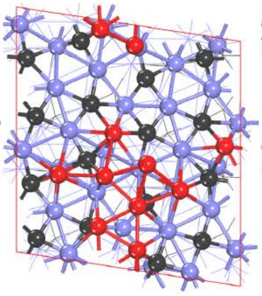
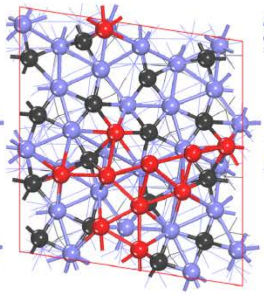
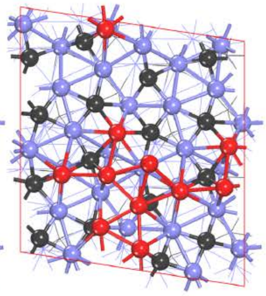
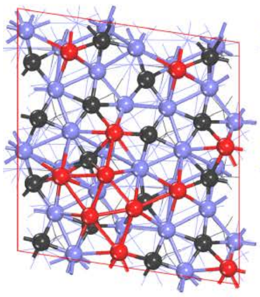
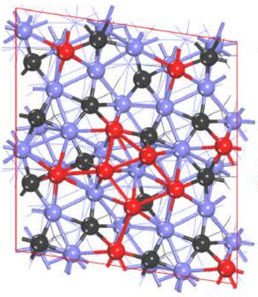
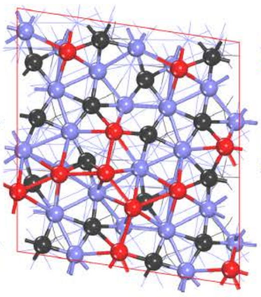

a7 (–34.87)

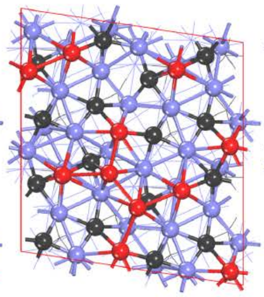

a8 (–34.84)

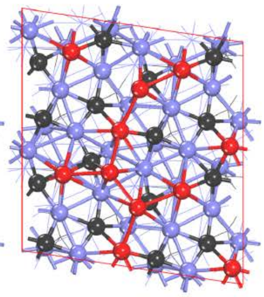

a9 (–34.81)

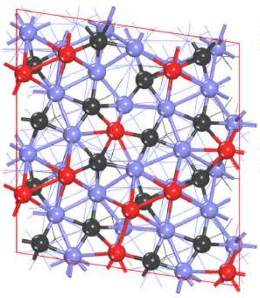

d1 (–35.32)


d2 (–34.93)


d3 (–34.84)


d4 (–34.81)


d5 (–34.76)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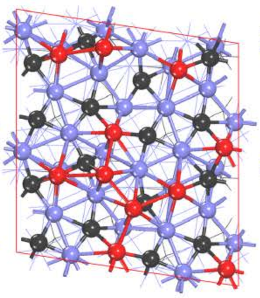
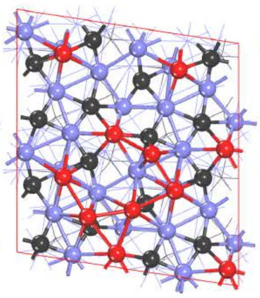
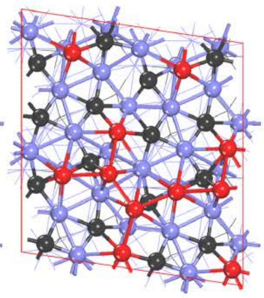
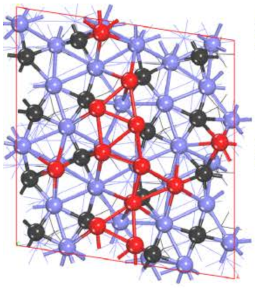
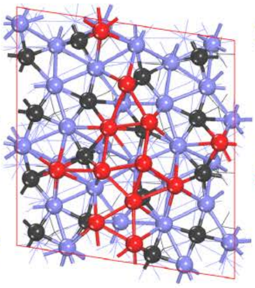

d7 (–34.53)

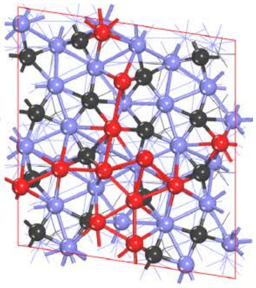

d8 (–34.46)

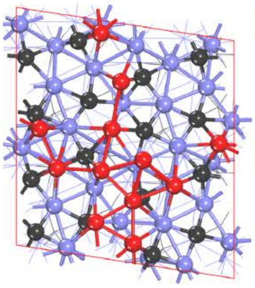

d9 (–34.44)

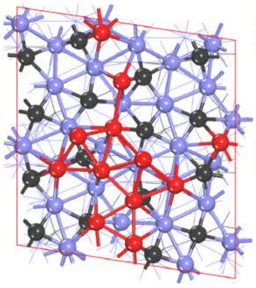
Cu12

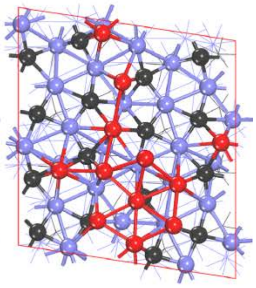

a1 (–38.19)

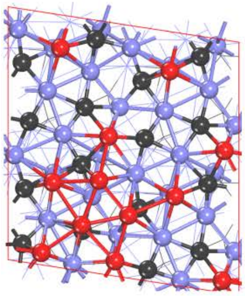

a2 (–38.14)

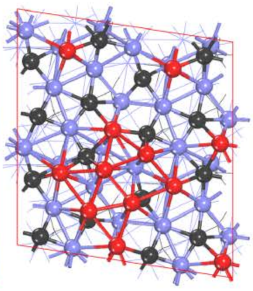

a3 (–37.86)

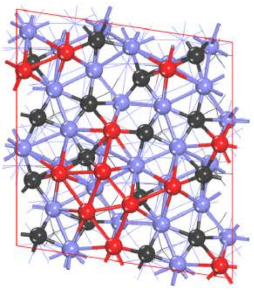

a4 (–37.84)

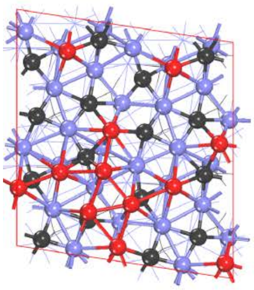

a5 (–37.83)

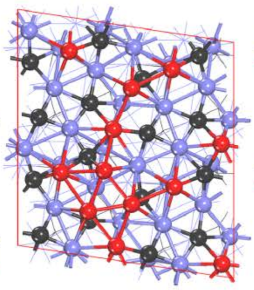

a6 (–37.82)

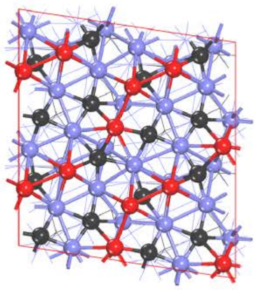

d1 (–38.50)

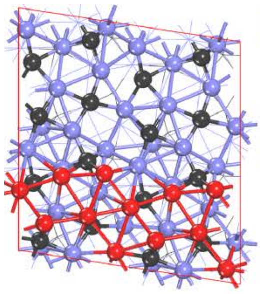

d2 (–38.47)


d3 (–38.36)

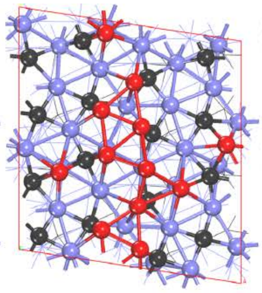

d4 (–38.36)


d5 (–38.30)

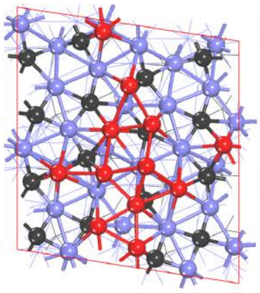

d6 (–37.56)



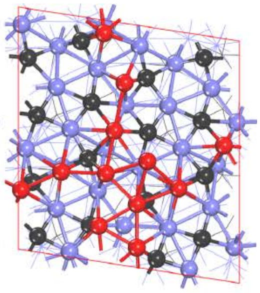
a1 (–38.22)



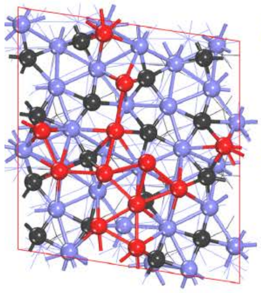
a2 (–38.19)



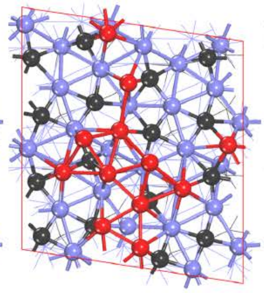
a3 (–38.14)



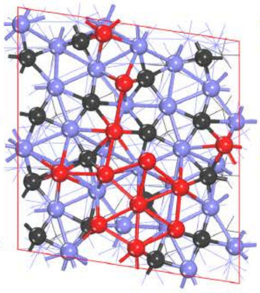
a4 (–37.86)



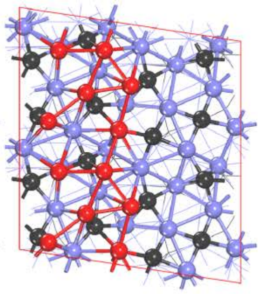
a5 (–37.84)



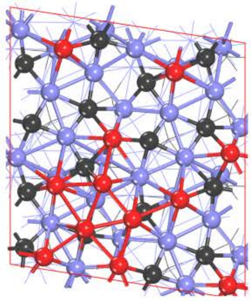
a6 (–37.83)



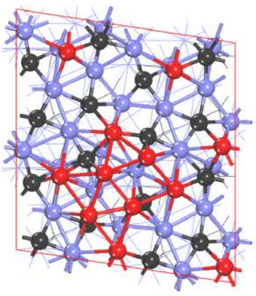
a7 (–37.82)



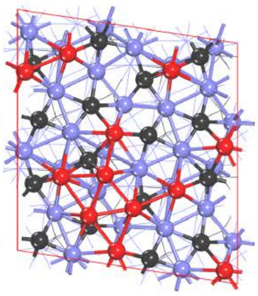
a8 (–37.48)



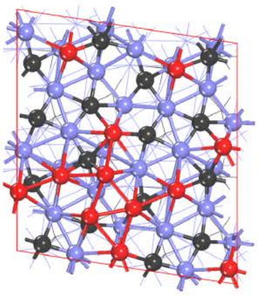
d1 (–38.50)



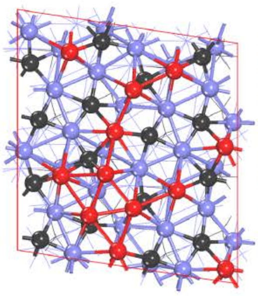
d2 (–38.47)



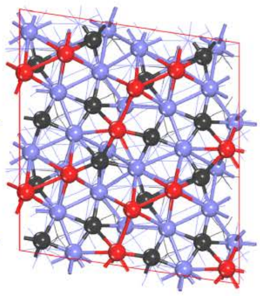
d3 (–38.36)



d4 (–38.36)

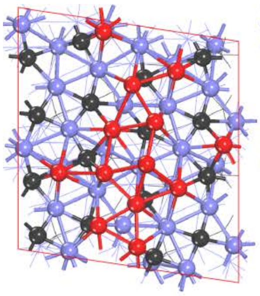


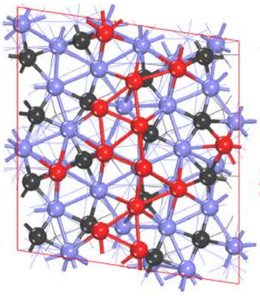
d5 (–38.30)

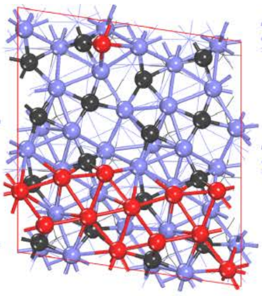


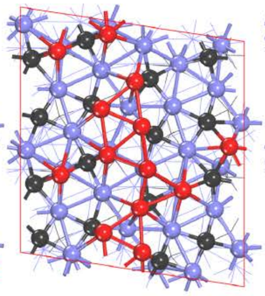
d6 (–37.56)

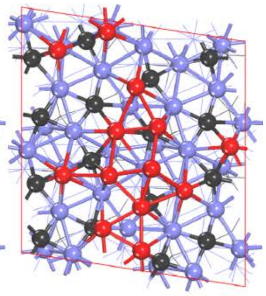
Cu13

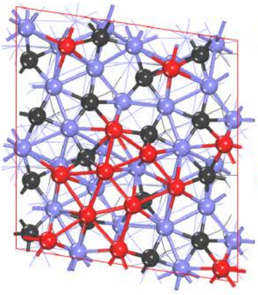

a1 (–41.66)

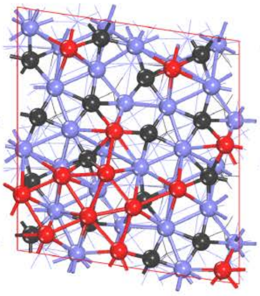

a2 (–41.61)

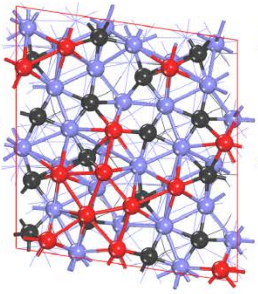

a3 (–41.18)

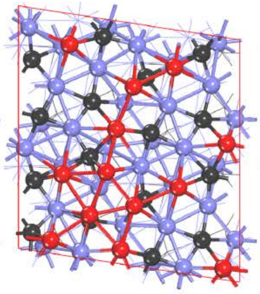

a4 (–41.10)

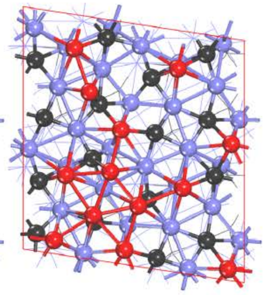

a5 (–41.02)

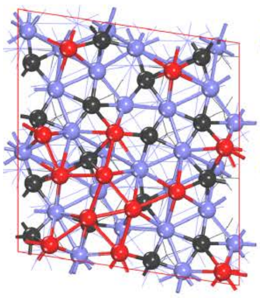

d1 (–41.63)

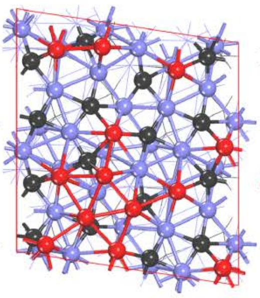

d2 (–41.57)

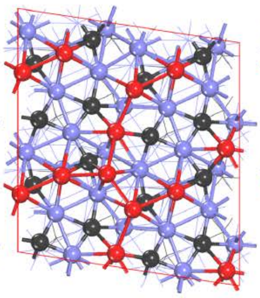

d3 (–41.56)

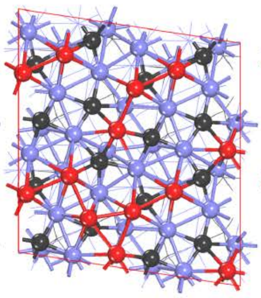

d4 (–41.54)

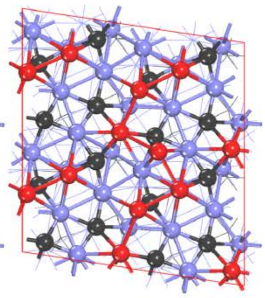

d5 (–41.39)


d6 (–41.24)

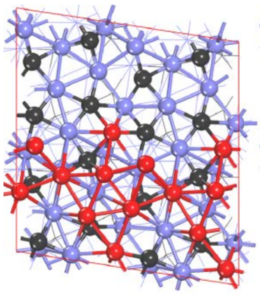

d7 (–41.09)

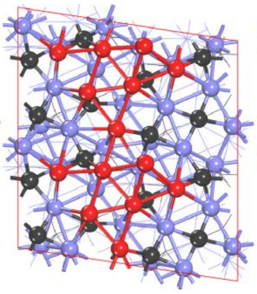

d8 (–40.81)

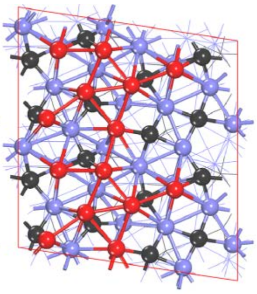

d9 (–40.76)


d10 (–40.50)

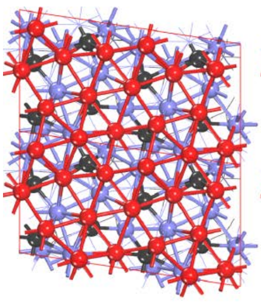
Cu14

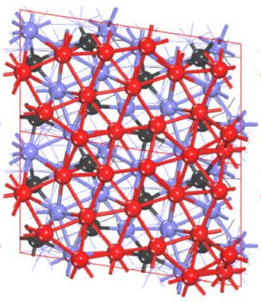

a1 (–45.04)

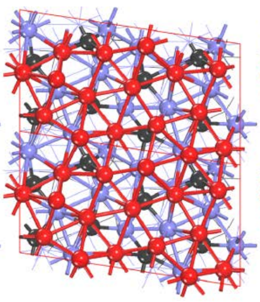

a2 (–44.75)


a3 (–44.23)

Cu16-*p*(2×1)-1ML


a1 (–53.24)


a2 (–52.90)


a3 (–52.80)

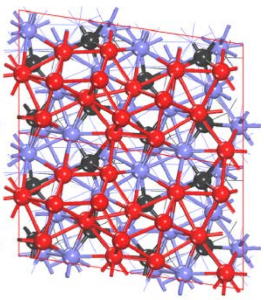

a4 (–51.96)

Figure S4. Diffusion pathways of single Cu atom on the $Fe_5C_2(111)$ surface

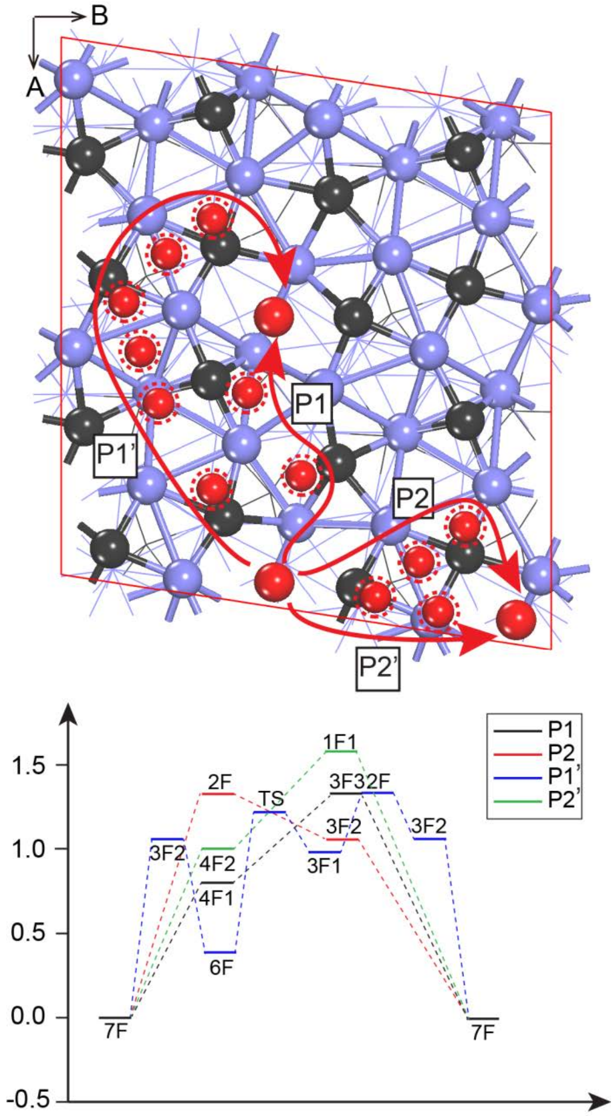
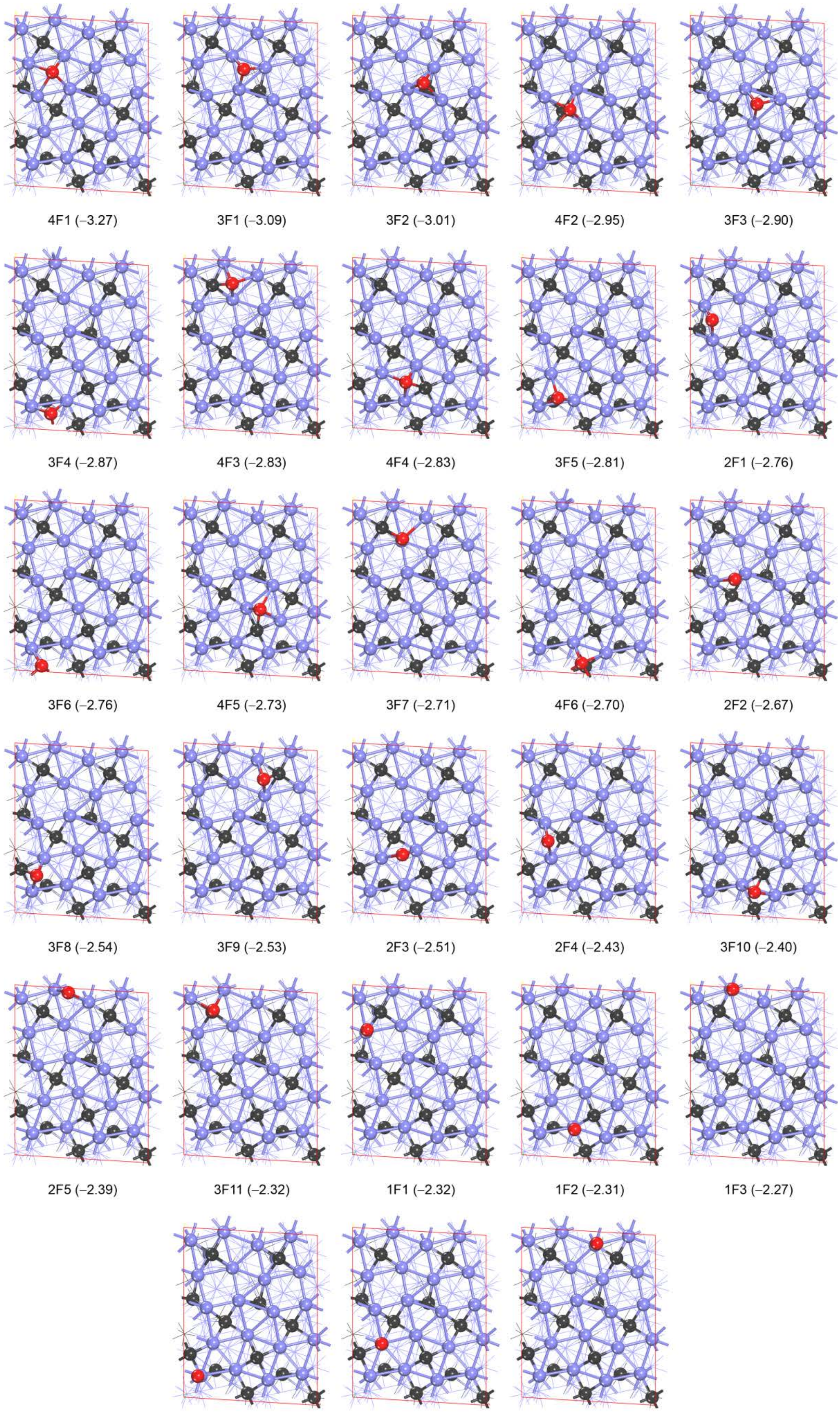


Figure S5. Various optimized $Cu_{1\text{-}17}$, Cu_{20} configurations on the $p(2\times1)$ $Fe_5C_2(510)$ surface (adsorption energy in eV)

Cu1



4F1 (–3.27) 3F1 (–3.09) 3F2 (–3.01) 4F2 (–2.95) 3F3 (–2.90)

3F4 (–2.87) 4F3 (–2.83) 4F4 (–2.83) 3F5 (–2.81) 2F1 (–2.76)

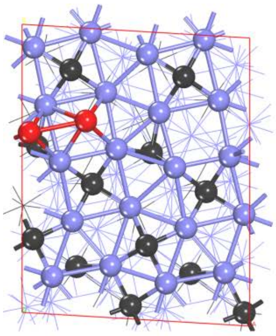
3F6 (–2.76) 4F5 (–2.73) 3F7 (–2.71) 4F6 (–2.70) 2F2 (–2.67)

3F8 (–2.54) 3F9 (–2.53) 2F3 (–2.51) 2F4 (–2.43) 3F10 (–2.40)

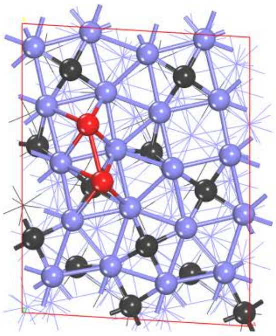
2F5 (–2.39) 3F11 (–2.32) 1F1 (–2.32) 1F2 (–2.31) 1F3 (–2.27)

1F4 (–2.09) 1F5 (–2.05) 1F6 (–1.92)

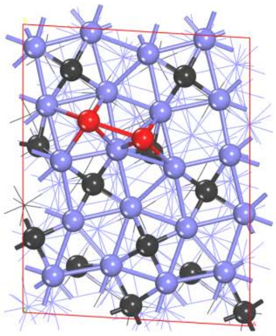
Cu2



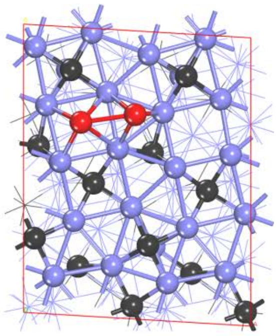
a1 (–6.50)



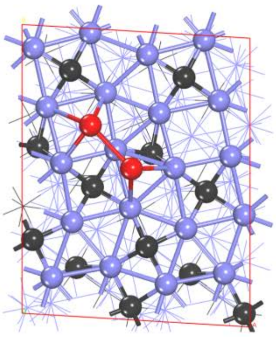
a2 (–6.46)



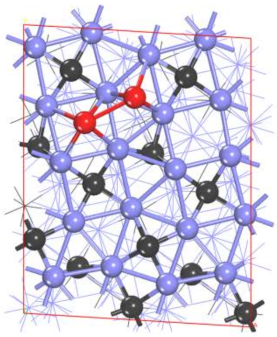
a3 (–6.45)



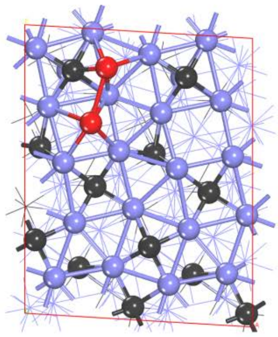
a4 (–6.35)



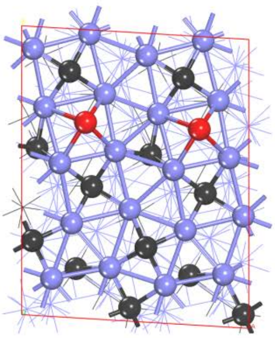
a5 (–6.35)



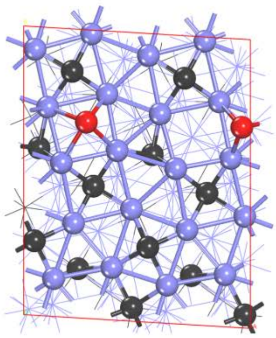
a6 (–6.34)



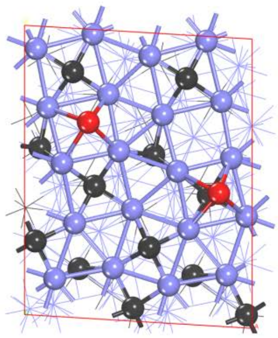
a7 (–6.26)



d1 (–6.50)

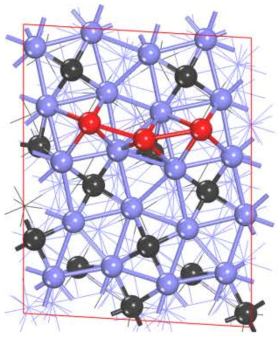


d2 (–6.40)

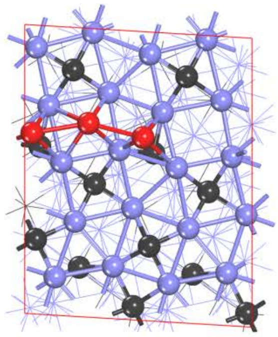


d3 (–6.20)

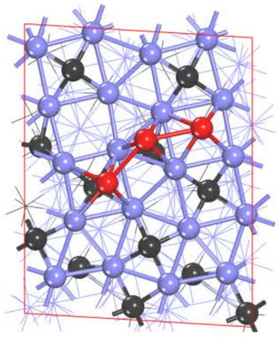
Cu3



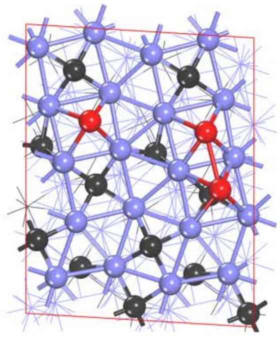
a1 (–9.99)



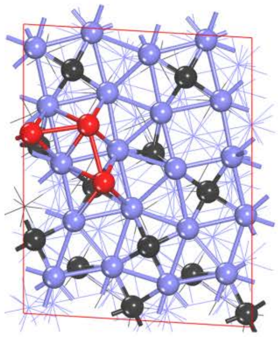
a2 (–9.73)



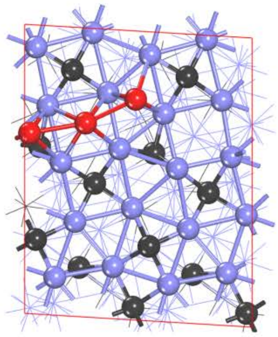
a3 (–9.72)



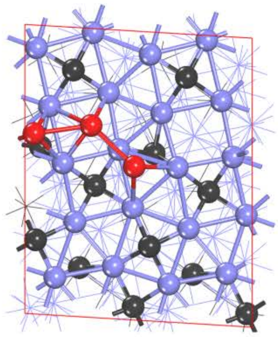
a4 (–9.68)



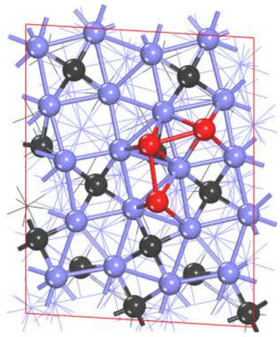
a5 (–9.66)



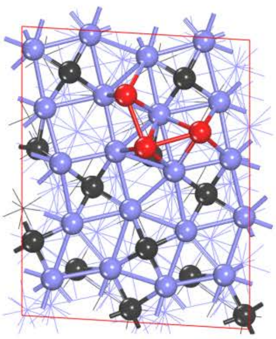
a6 (–9.63)



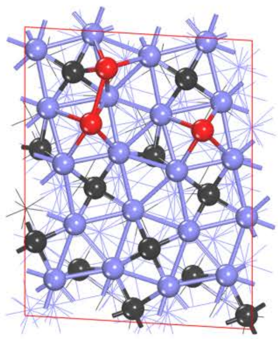
a7 (–9.57)



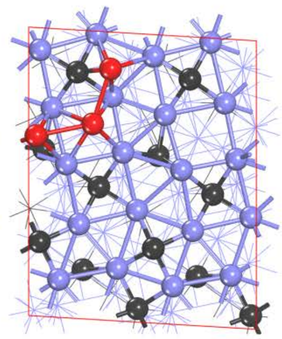
a8 (–9.53)



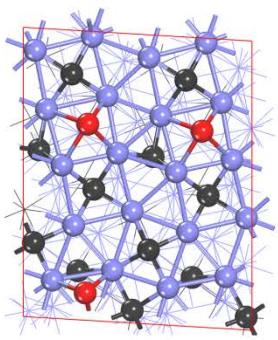
a9 (–9.53)



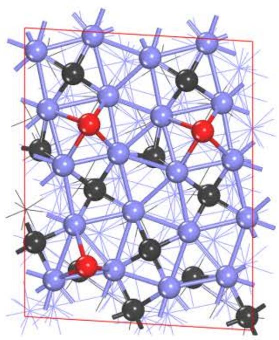
a10 (–9.50)



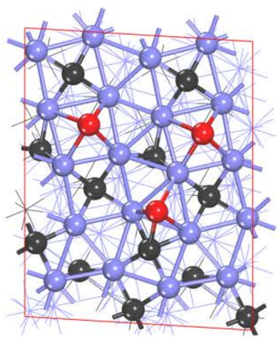
a11 (–9.49)



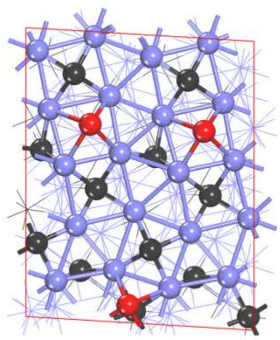
d1 (–9.36)



d2 (–9.29)

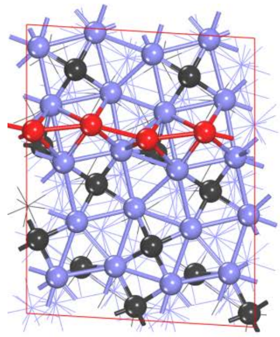


d3 (–9.24)

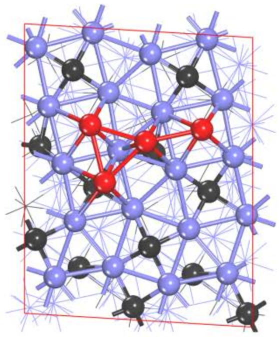


d4 (–9.18)

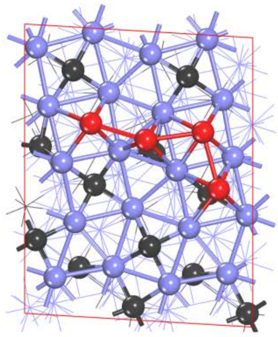
Cu4



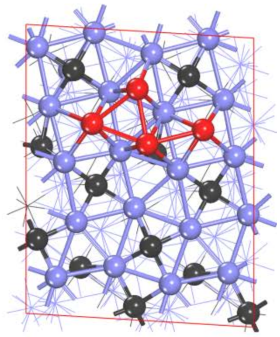
a1 (–13.54)



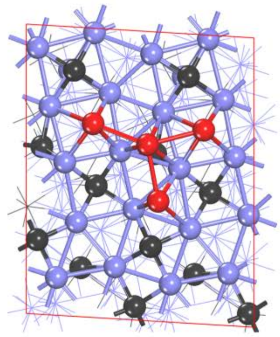
a2 (–13.36)



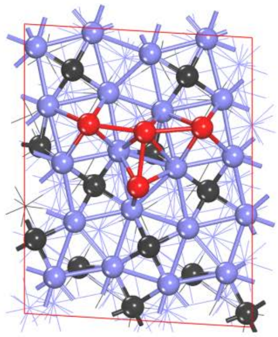
a3 (–13.16)



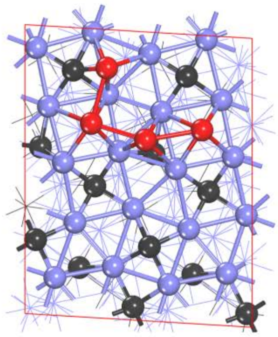
a4 (–13.15)



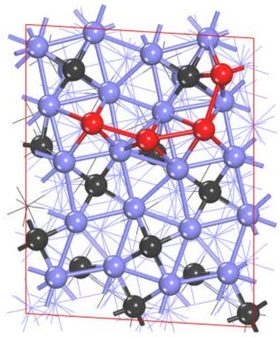
a5 (–13.02)



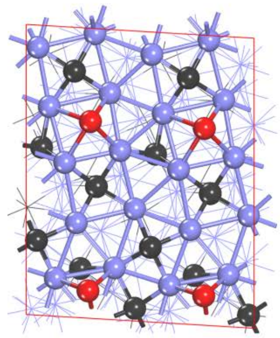
a6 (–12.99)



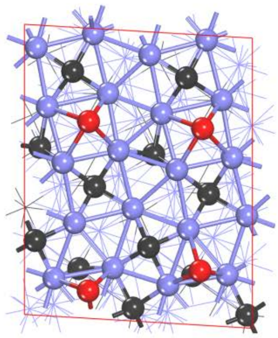
a7 (–12.98)



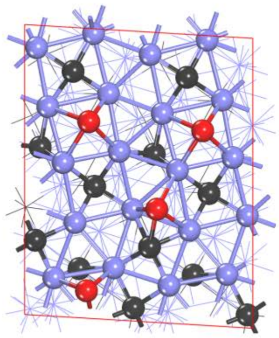
a8 (–12.98)



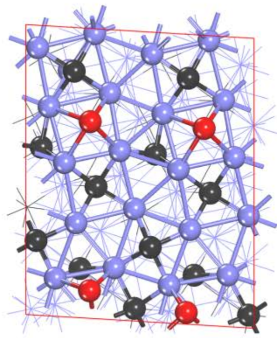
d1 (–12.17)



d2 (–12.11)

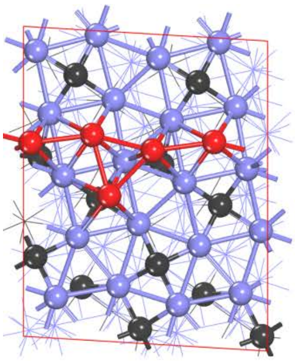


d3 (–12.07)

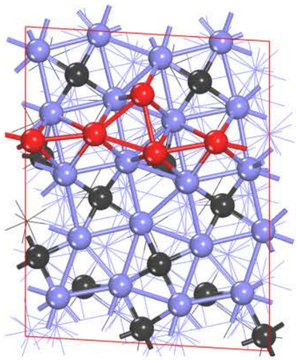


d4 (–12.07)

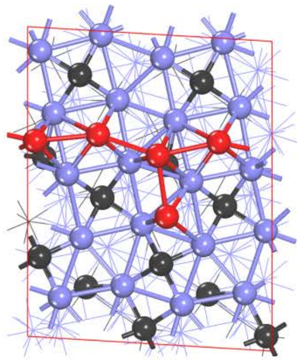
Cu5



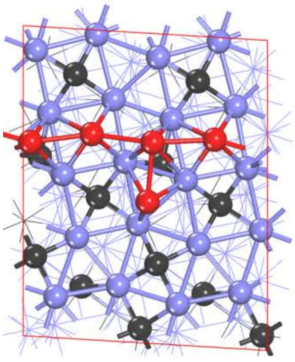
a1 (–16.88)



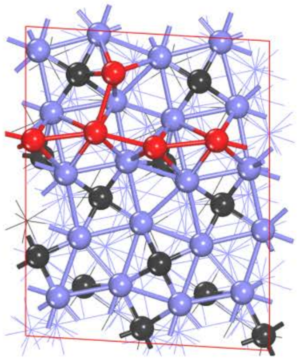
a2 (–16.71)



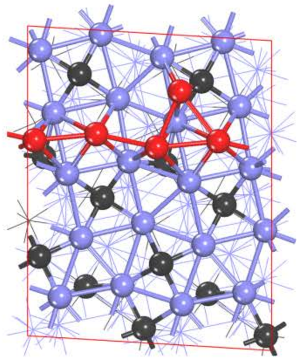
a3 (–16.55)



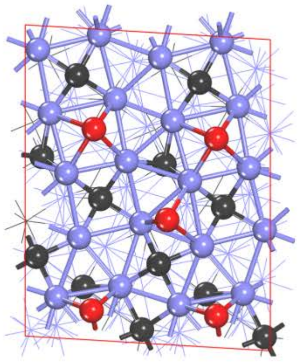
a4 (–16.54)



a5 (–16.51)

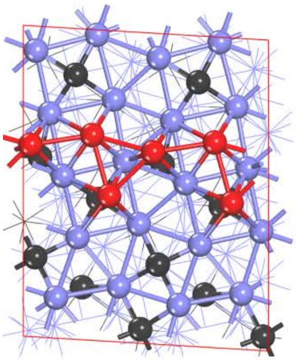


a6 (–16.51)

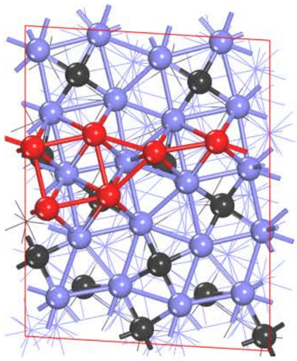


d1 (–14.88)

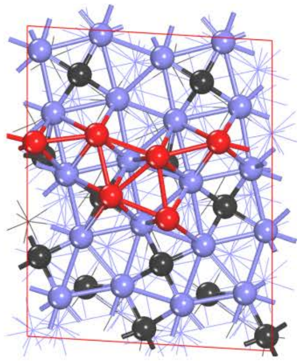
Cu6



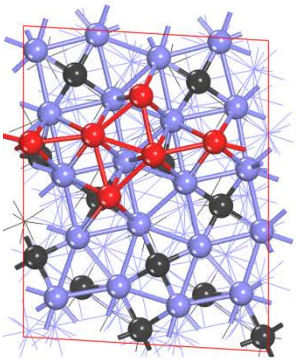
a1 (–20.25)



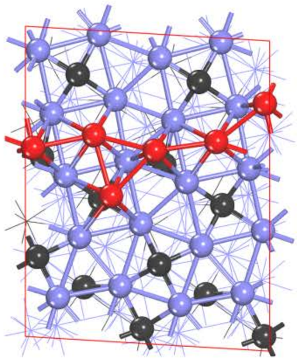
a2 (–20.15)



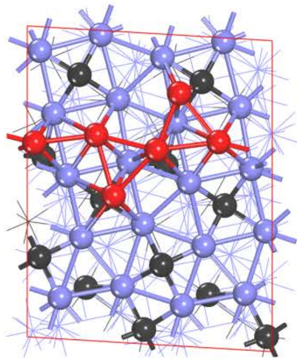
a3 (–20.14)



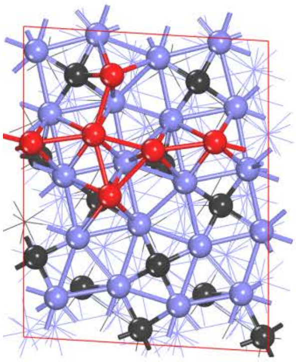
a4 (–20.10)



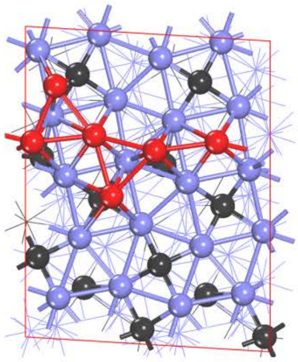
a5 (–20.07)



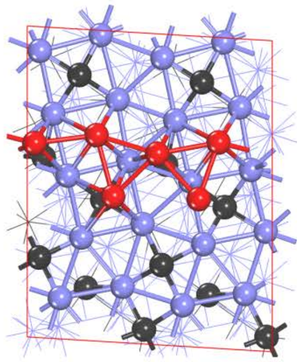
a6 (–19.90)



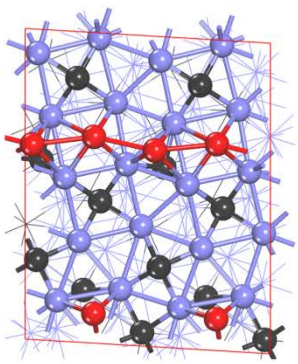
a7 (–19.89)



a8 (–19.87)

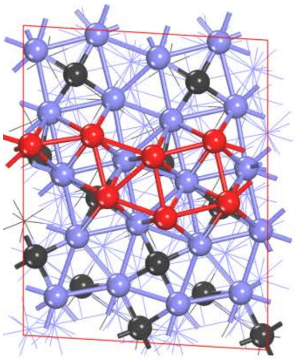


a9 (–19.81)

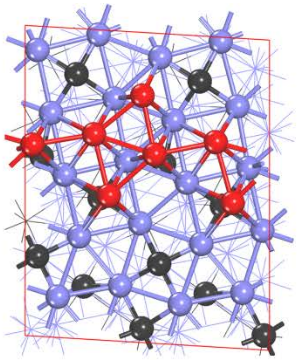


d1 (–19.19)

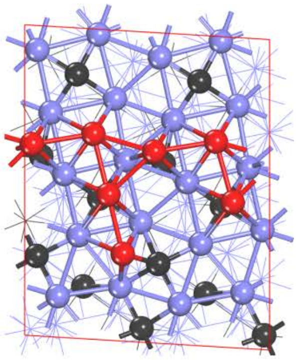
Cu7



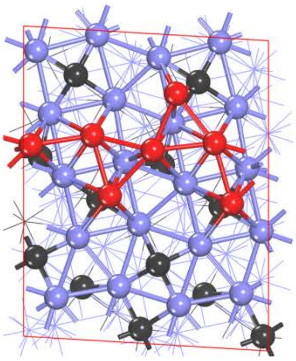
a1 (–23.78)



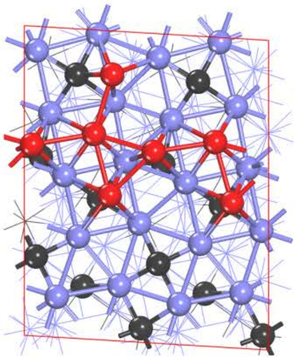
a2 (–23.47)



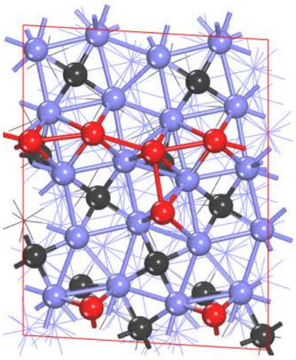
a3 (–23.43)



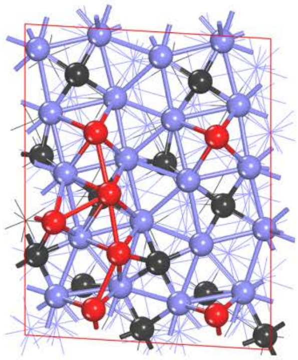
a4 (–23.27)



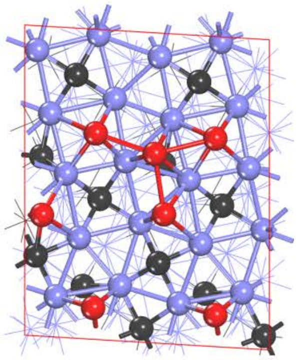
a5 (–23.24)



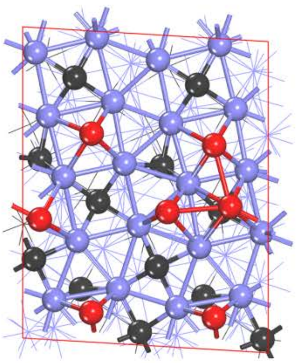
d1 (–22.19)



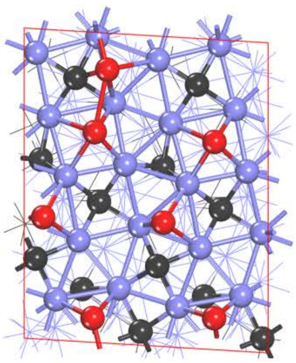
d2 (–21.74)



d3 (–21.39)

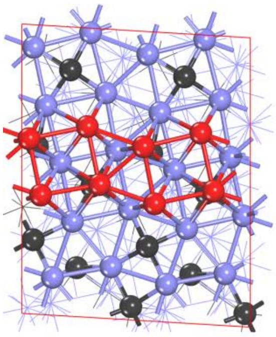


d4 (–21.38)

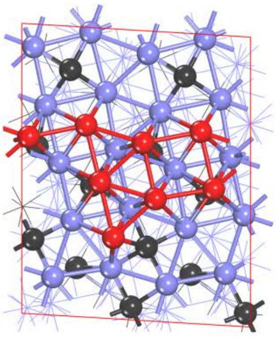


d5 (–20.85)

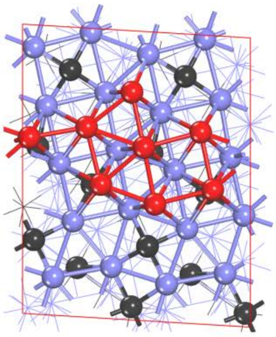
Cu8



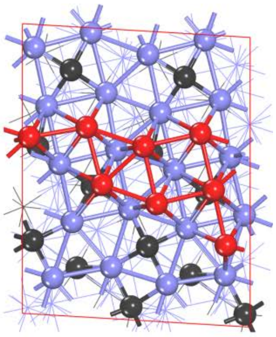
a1 (–27.33)



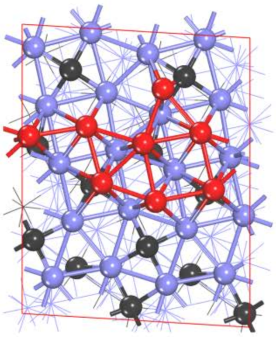
a2 (–27.13)



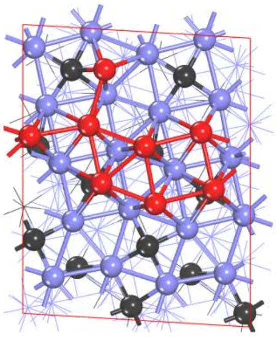
a3 (–27.05)



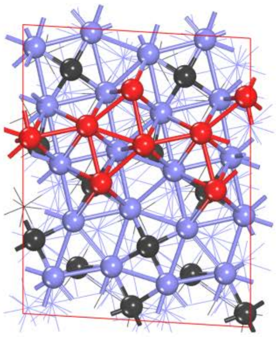
a4 (–27.00)



a5 (–26.78)

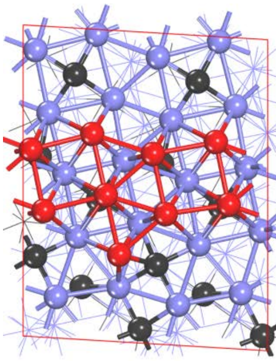


a6 (–26.74)

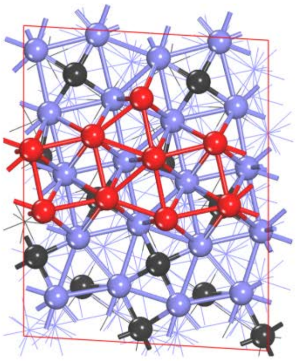


a7 (–26.70)

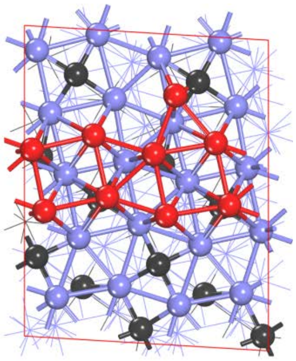
Cu9



a1 (–30.73)

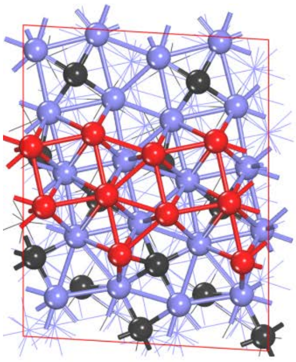


a2 (–30.61)

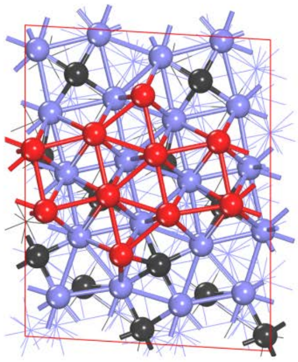


a3 (–30.32)

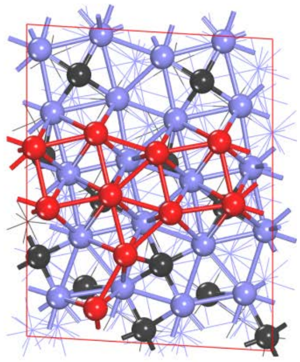
Cu10



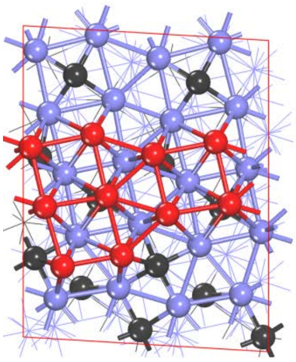
a1 (–34.11)



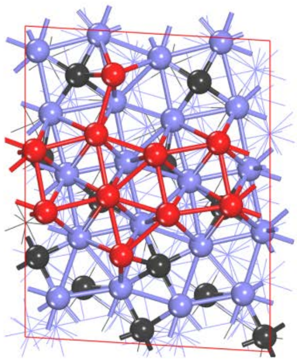
a2 (–33.97)



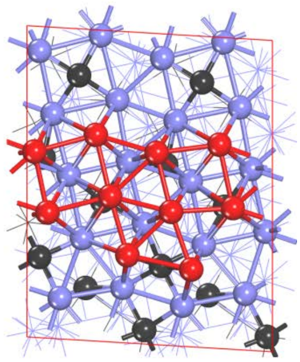
a3 (–33.84)



a4 (–33.78)

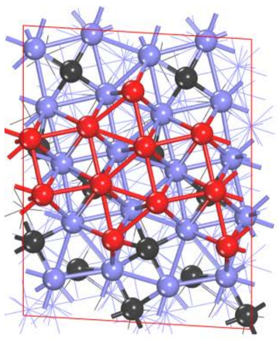


a5 (–33.70)

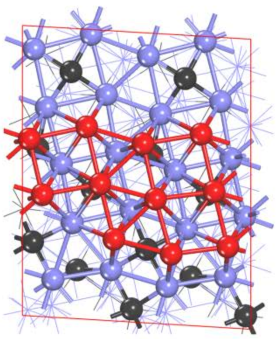


a6 (–33.70)

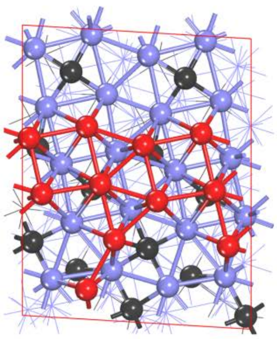
Cu11



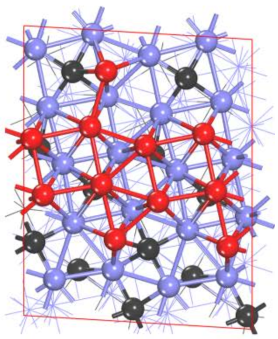
a1 (–37.35)



a2 (–37.33)

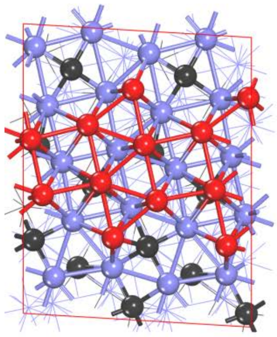


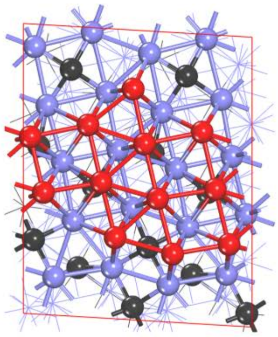
a3 (–37.23)

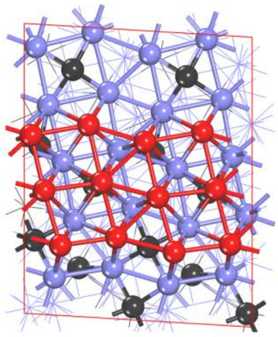


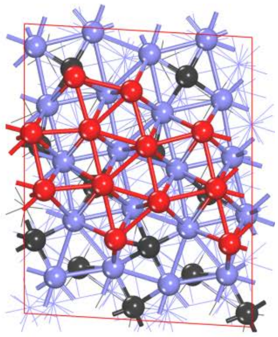
a4 (–37.08)

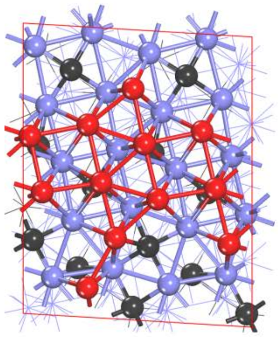
Cu12

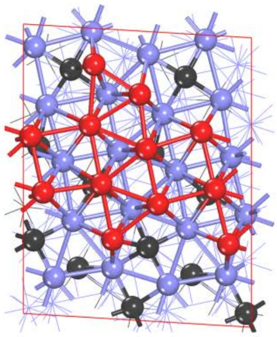

a1 (–40.62)

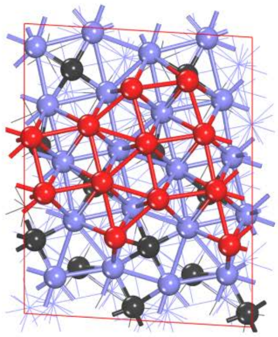

a2 (–40.57)

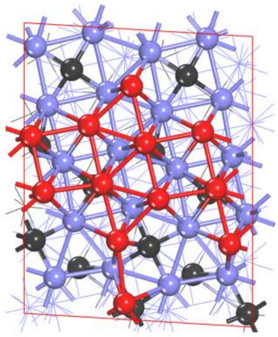

a3 (–40.55)


a4 (–40.50)

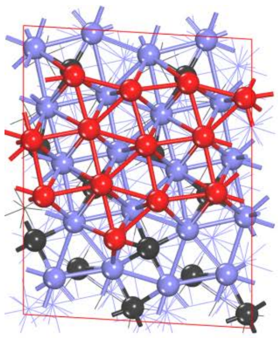

a5 (–40.48)

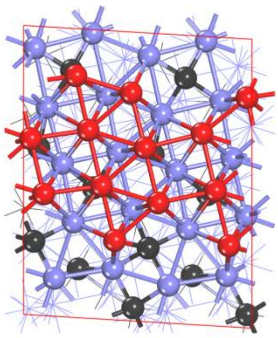

a6 (–40.47)

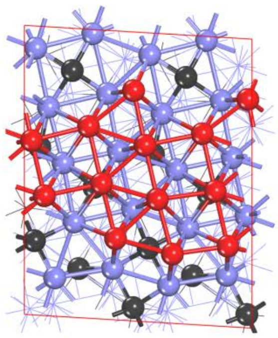

a7 (–40.40)

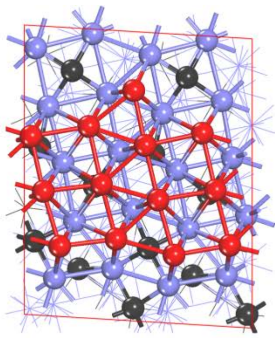

a8 (–40.38)

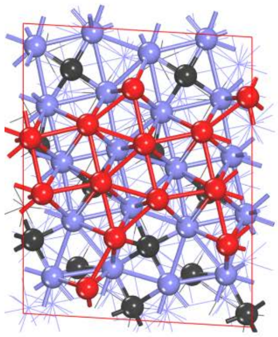
Cu13

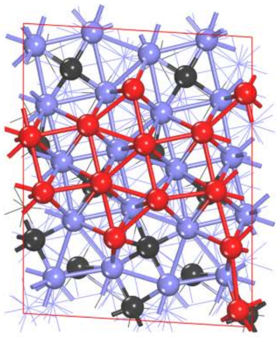

a1 (–44.04)

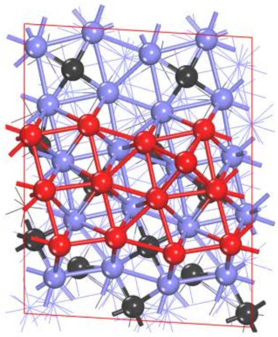

a2 (–43.99)

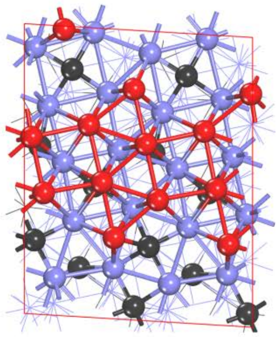

a3 (–43.83)


a4 (–43.80)

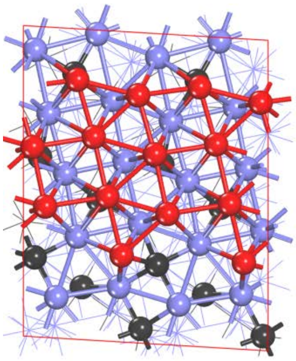

a5 (–43.74)


a6 (–43.64)

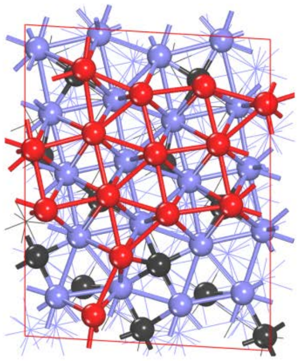

a7 (–43.44)


a8 (–43.43)

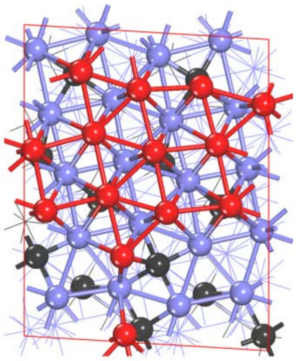
Cu14



a1 (–47.41)

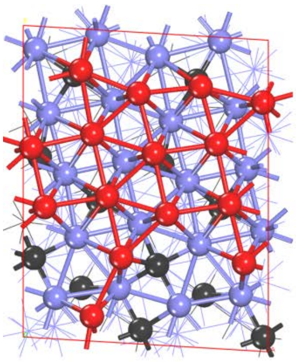


a2 (–47.40)

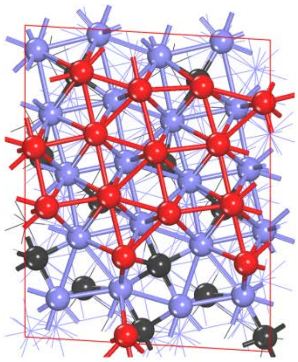


a3 (–47.29)

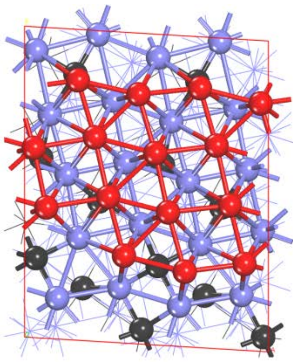
Cu15



a1 (–50.76)

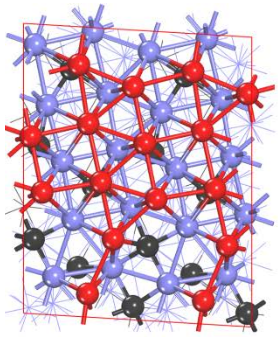


a2 (–50.66)

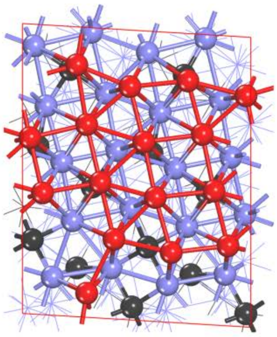


a3 (–50.63)

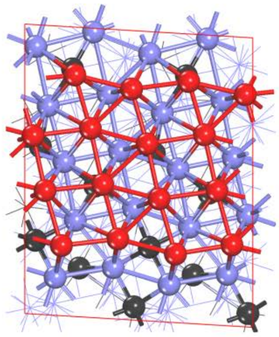
Cu16



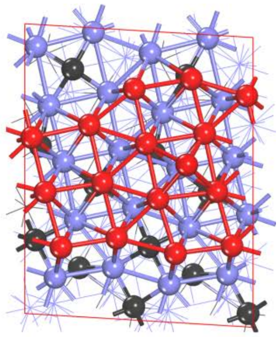
a1 (–54.11)



a2 (–53.99)

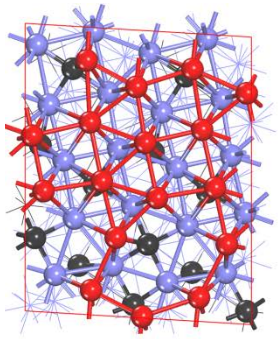


a3 (–53.86)

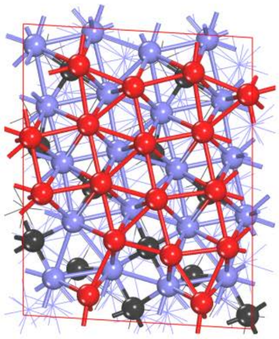


a4 (–53.33)

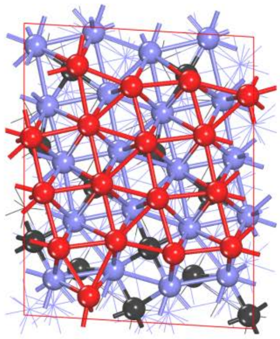
Cu17



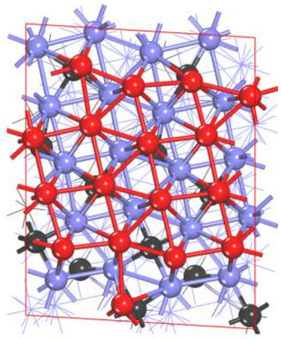
a1 (–57.76)



a2 (–57.63)

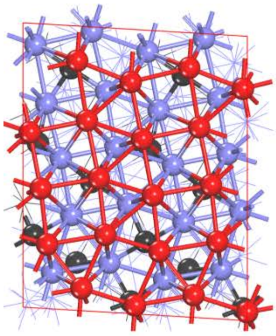


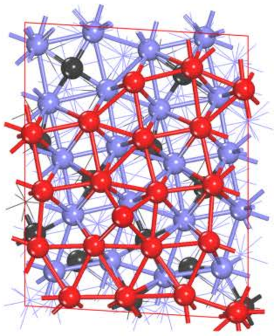
a3 (–57.51)

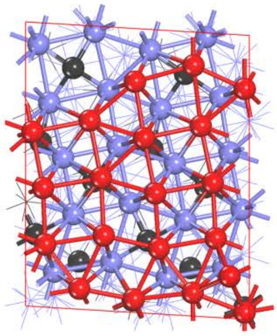


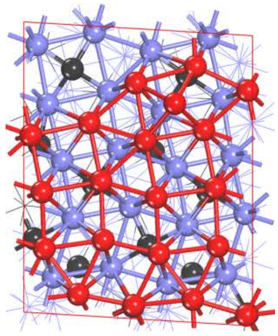
a4 (–57.26)

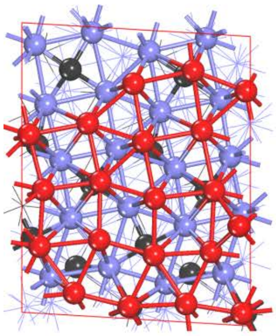
Cu20

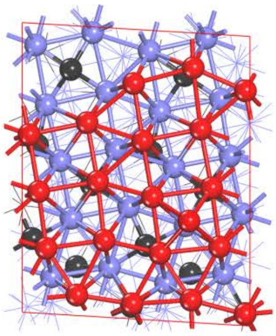

a1 (–68.94)

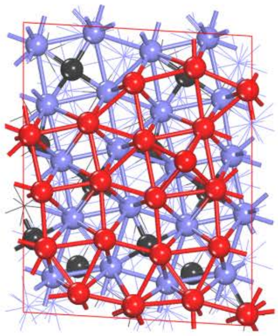

a2 (–68.28)

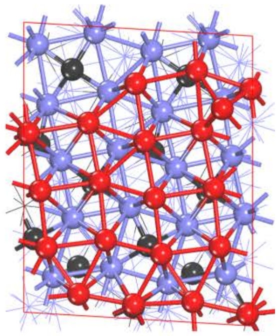

a3 (–68.28)

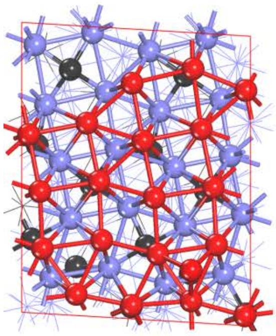

a4 (–68.20)

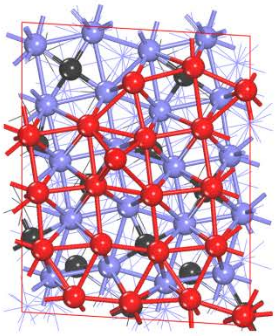

a5 (–68.15)

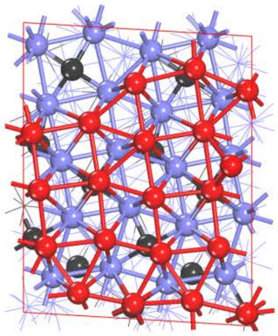

a6 (–68.13)

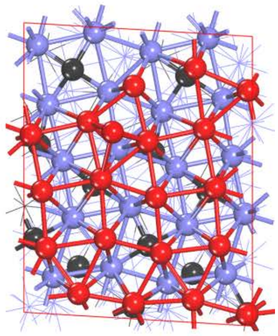

a7 (–68.03)

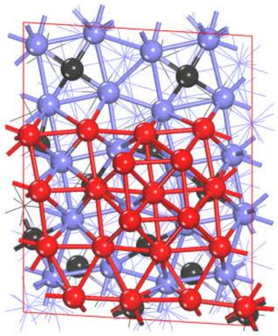

a8 (–67.96)

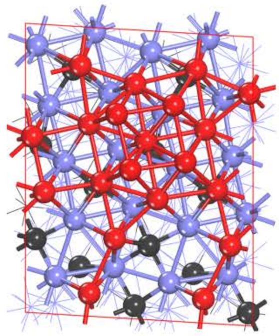

a9 (–67.87)


a10 (–67.83)


a11 (–67.79)


a12 (–67.78)


a13 (–66.95)


a14 (–66.80)

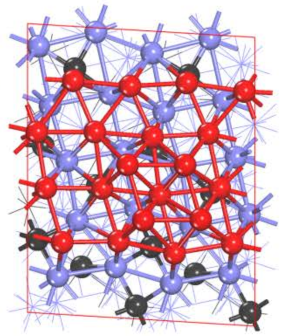

a15 (–66.44)

Figure S6. Diffusion pathways of single Cu atom on the Fe_5C_2(510) surface

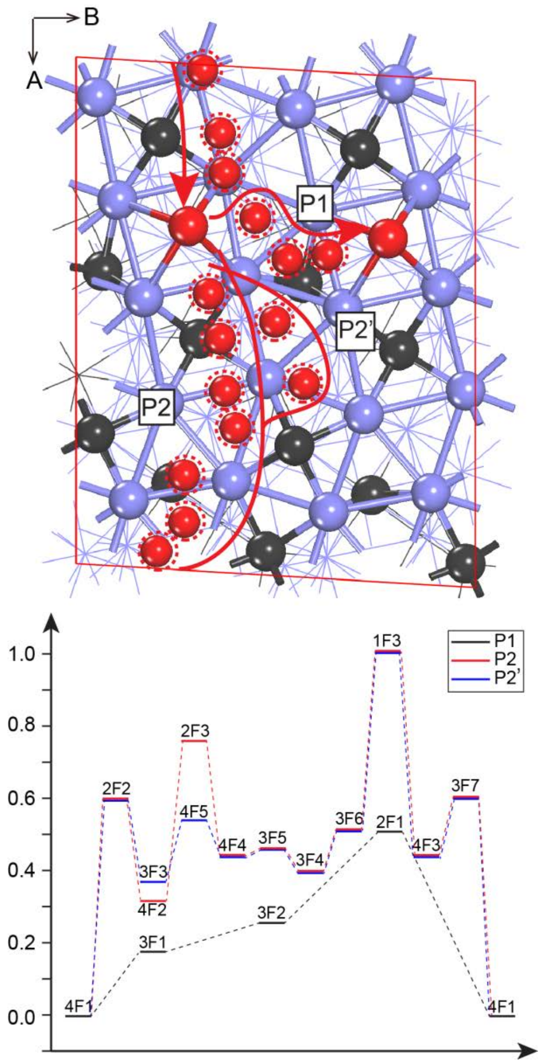
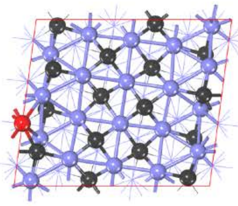
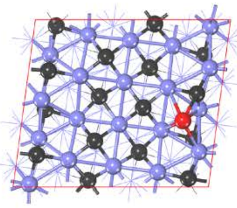


Figure S7. Various optimized $Cu_{1\text{-}7}$, Cu_{12}, Cu_{14}, Cu_{16}, Cu_{18}, Cu_{19}, Cu_{20} configurations on the *p*(2×1) Fe_5C_2(010) surface (adsorption energy in eV)

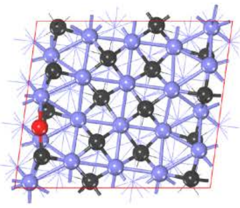
Cu1



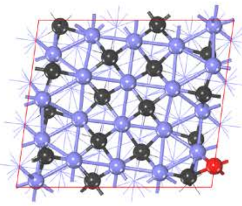
6F (–3.53)



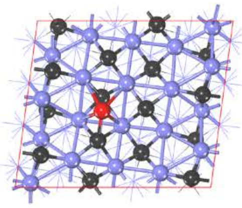
5F1 (–3.30)



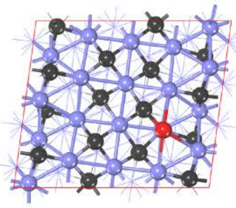
3F1 (–3.09)



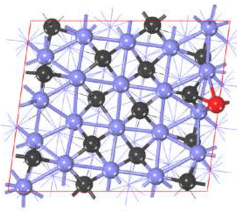
4F1 (–3.05)



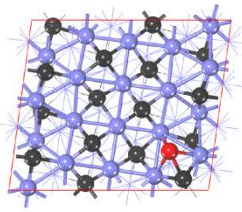
5F2 (–2.86)



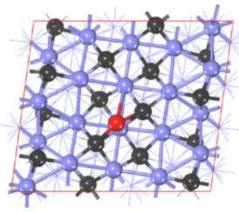
5F3 (–2.73)



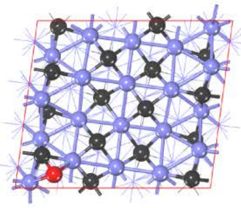
4F2 (–2.67)



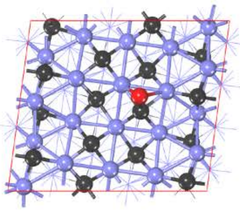
4F3 (–2.65)



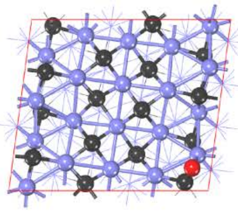
4F4 (–2.59)



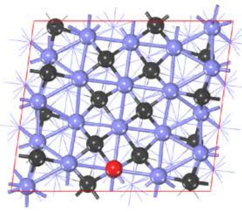
3F2 (–2.57)



3F3 (–2.40)

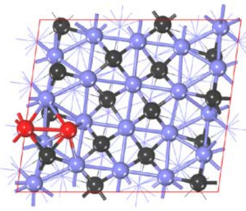


2F (–2.39)

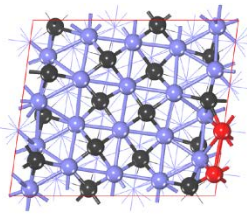


1F (–1.94)

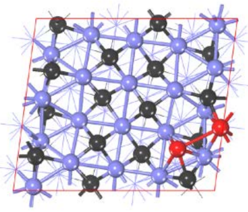
Cu2



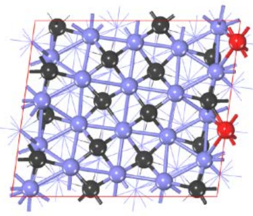
a1 (–6.88)



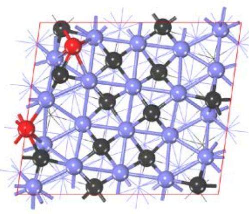
a2 (–6.78)



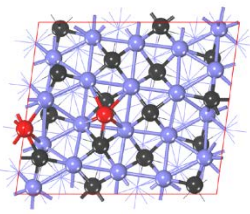
a3 (–6.41)



d1 (–7.15)

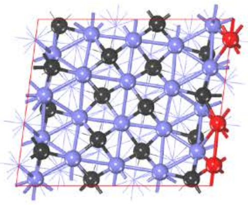


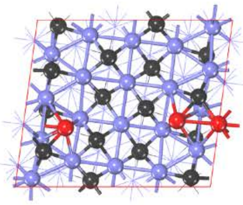
d2 (–6.83)

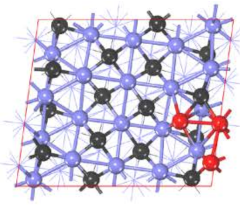


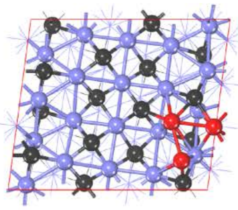
d3 (–6.42)

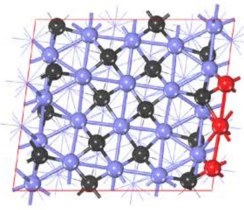
Cu3

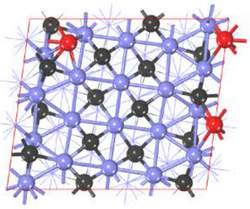

a1 (–10.70)

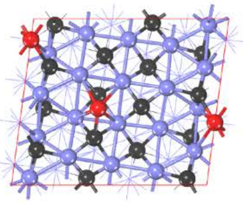

a2 (–10.21)


a3 (–10.09)

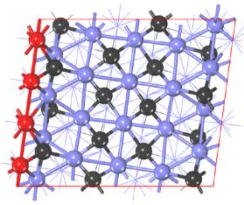

a4 (–9.99)

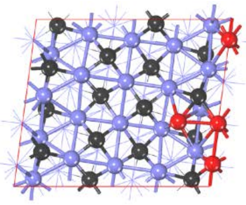

a5 (–9.95)

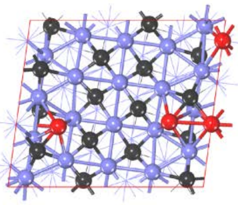

d1 (–10.56)

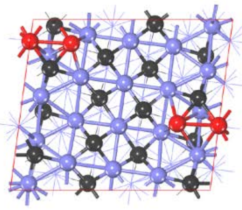

d2 (–10.06)

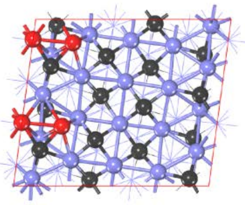
Cu4

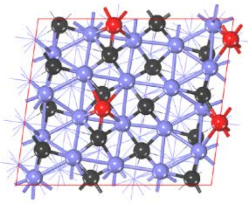

a1 (–14.17)


a2 (–14.14)

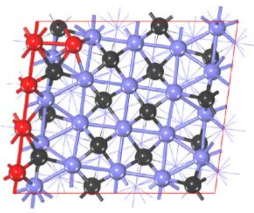

d1 (–14.00)


d2 (–13.88)

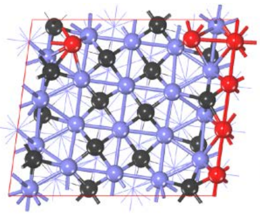

d3 (–13.82)

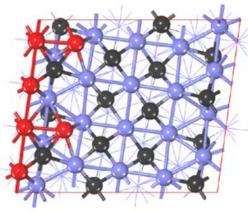

d4 (–12.89)

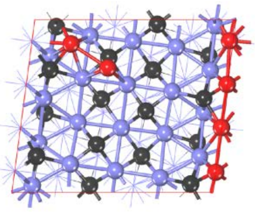
Cu5


a1 (–17.63)

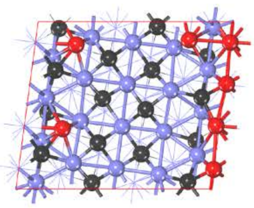
Cu6

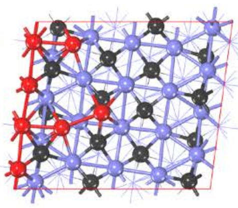

a1 (–21.09)

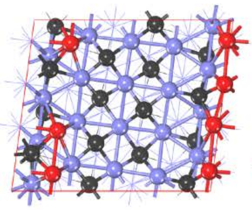

a2 (–21.01)

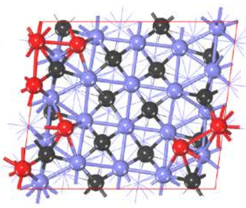

a3 (–20.10)

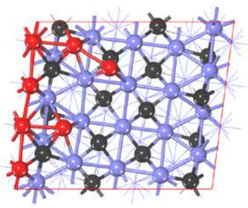
Cu7


a1 (–24.42)

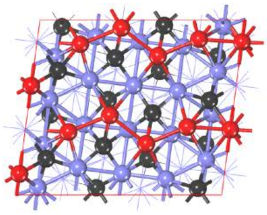

a2 (–24.08)

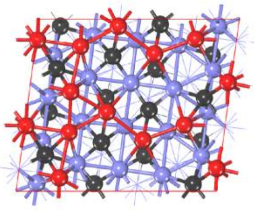

a3 (–24.07)

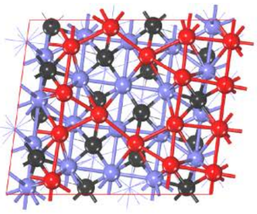

a4 (–23.94)

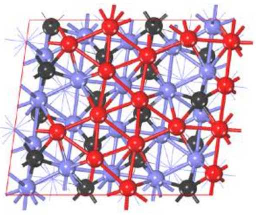

a5 (–23.50)

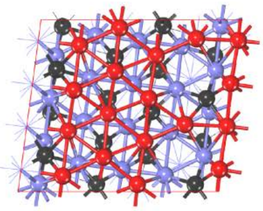
Cu12-19

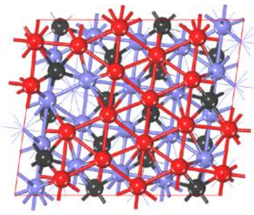

Cu12 (–40.01)

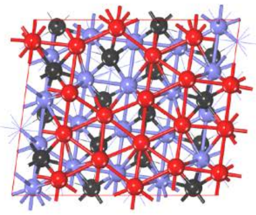

Cu14 (–47.20)


Cu16 (–54.20)

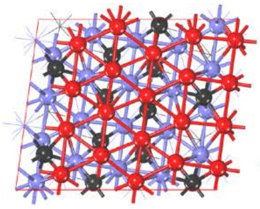

Cu16 (–54.15)

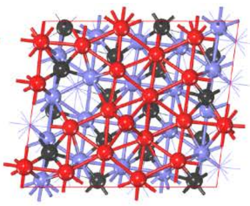

Cu18 (–61.83)

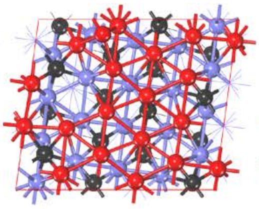

Cu19 (–65.64)

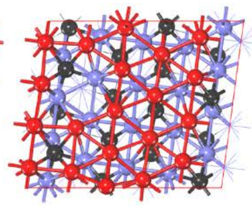

Cu19 (–65.46)

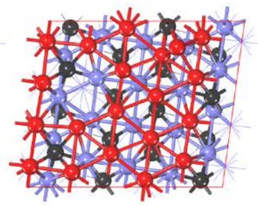
Cu20

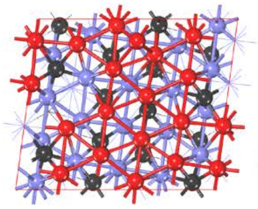

1 (–69.43)

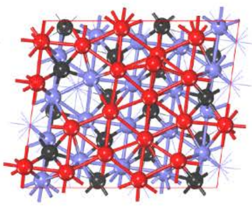

2 (–68.73)

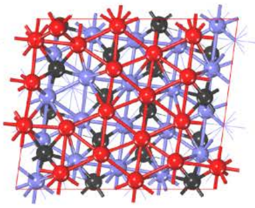

3 (–68.71)

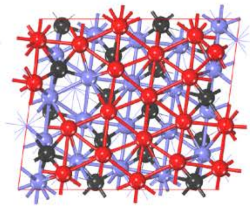

4 (–68.71)

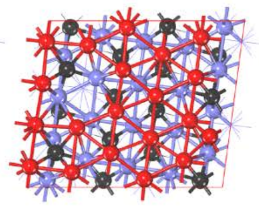

5 (–68.70)

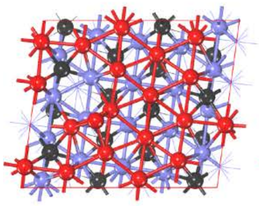

6 (–68.69)

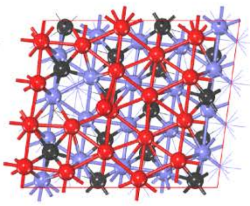

7 (–68.68)

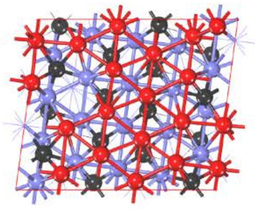

8 (–68.54)

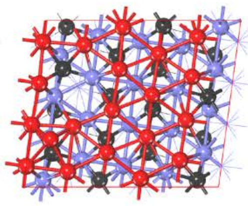

9 (–68.53)

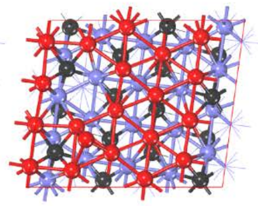

10 (–68.51)

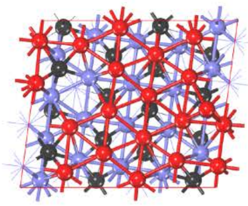

11 (–68.46)

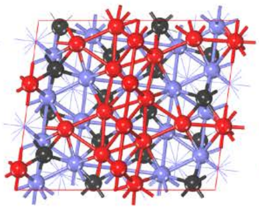

12 (–68.36)


13 (–68.33)


14 (–68.32)


15 (–68.31)


16 (–68.30)


17 (–66.61)

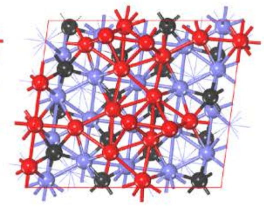

18 (–66.11)

Figure S8. Diffusion pathways of single Cu atom on the $Fe_5C_2(010)$ surface

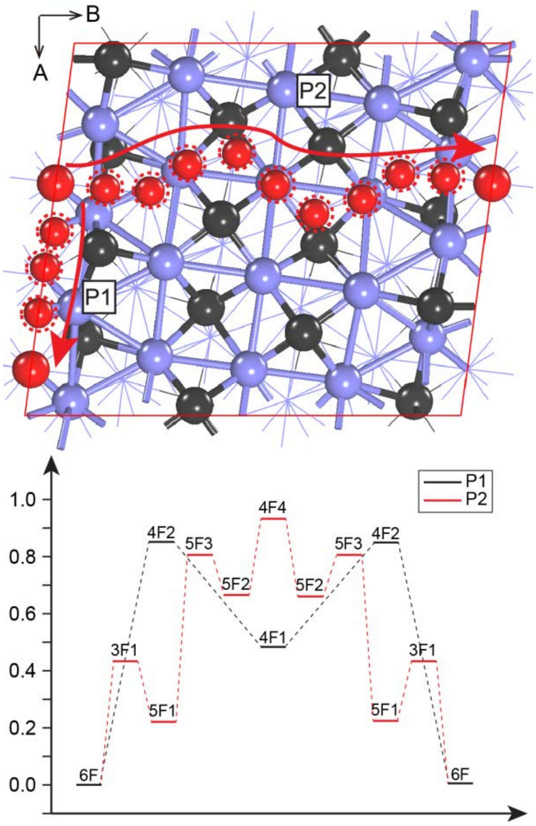
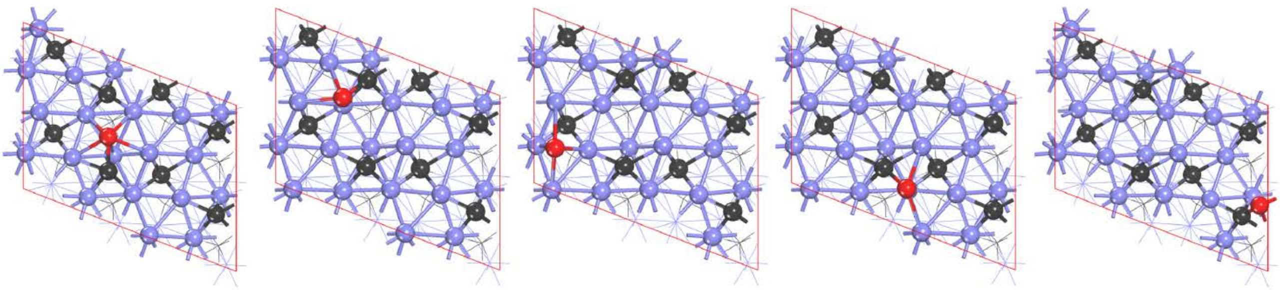
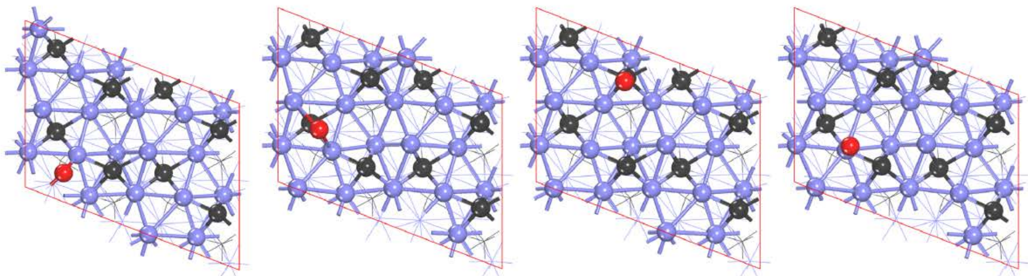


Figure S9. Various optimized $Cu_{1\text{-}7}$, Cu_{13}, Cu_{14}, Cu_{16}, Cu_{19}, Cu_{20} configurations on the p(2×1) Fe_5C_2(001) surface (adsorption energy in eV)

Cu1

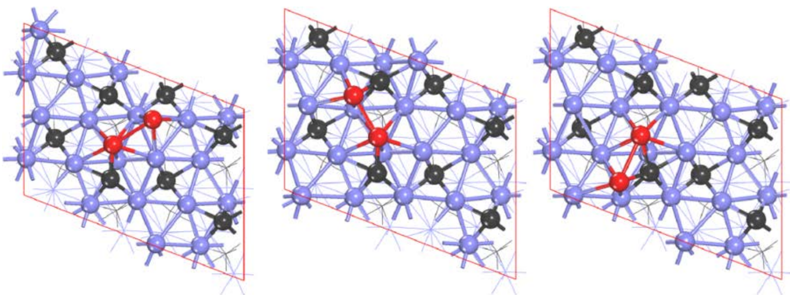


6F (–3.53) 4F1 (–3.06) 4F2 (–2.98) 4F3 (–2.94) 3F (–2.68)

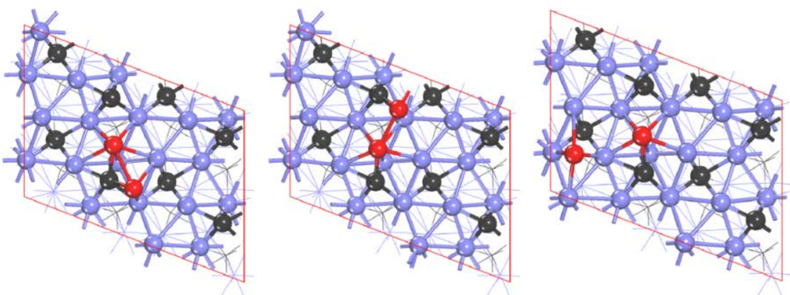


2F1 (–2.59) 2F2 (–2.54) 1F1 (–2.40) 1F2 (–2.17)

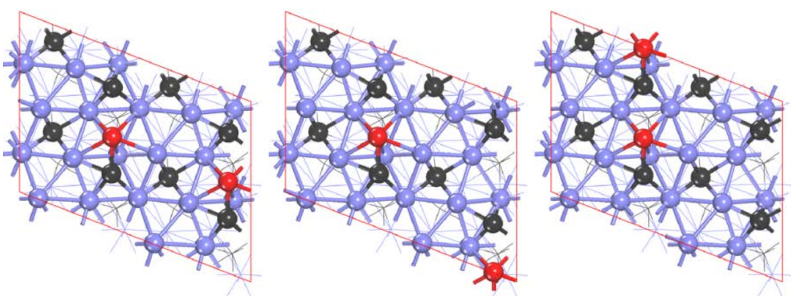
Cu2



a1 (–6.70) a2 (–6.70) a3 (–6.66)

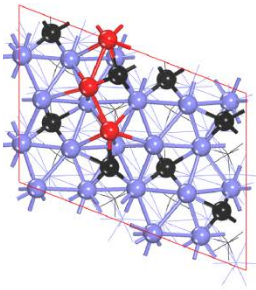


a4 (–6.57) a5 (–6.54) a6 (–6.50)

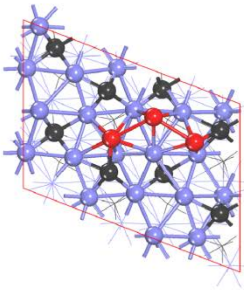


d1 (–7.00) d2 (–6.99) d3 (–6.95)

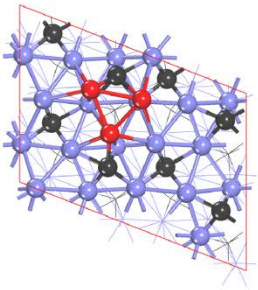
Cu3



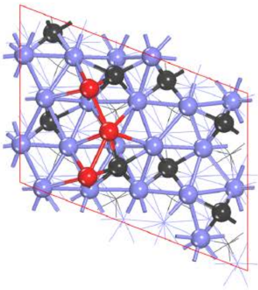
a1 (–10.29)



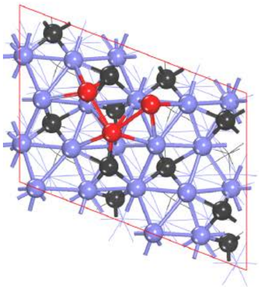
a2 (–10.11)



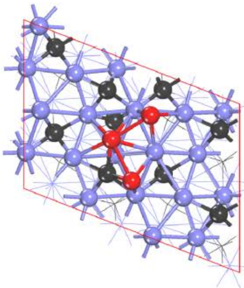
a3 (–9.92)



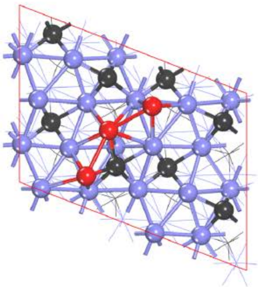
a4 (–9.90)



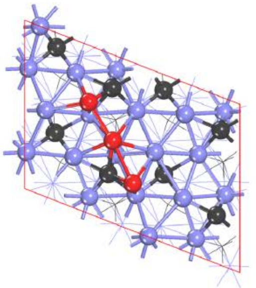
a5 (–9.90)



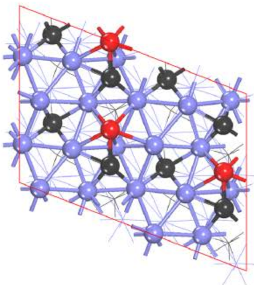
a6 (–9.79)



a7 (–9.78)

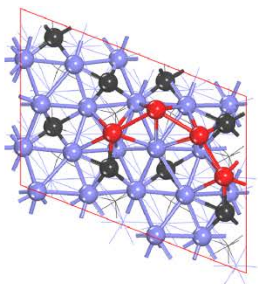


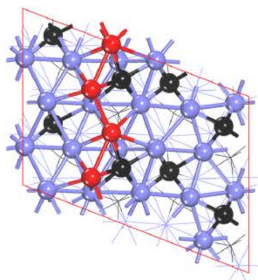
a8 (–9.73)

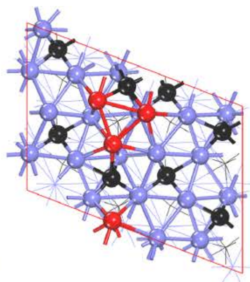


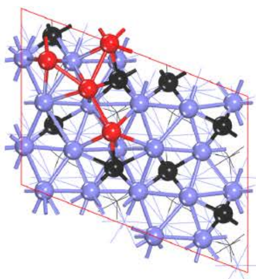
d1 (–10.44)

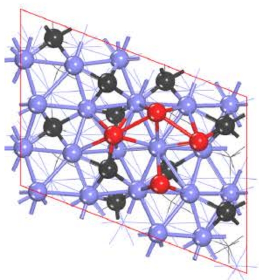
Cu4

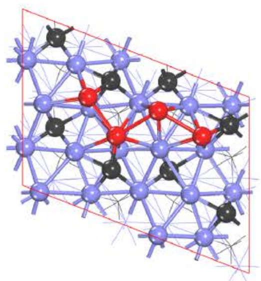

a1 (–13.70)

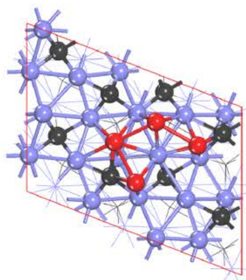

a2 (–13.66)

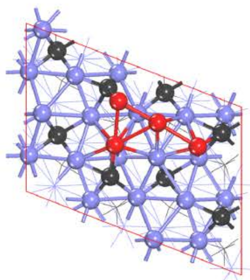

a3 (–13.61)

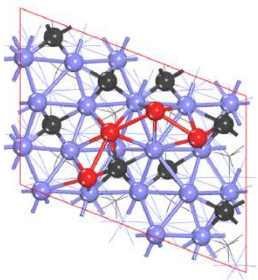

a4 (–13.57)

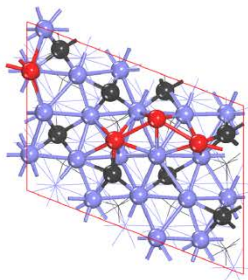

a5 (–13.28)

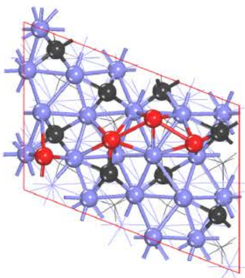

a6 (–13.26)

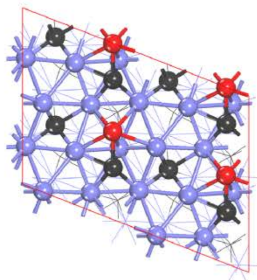

a7 (–13.25)

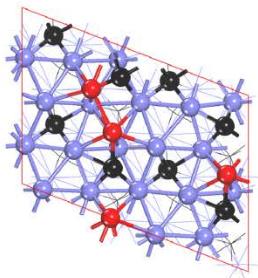

a8 (–13.23)


a9 (–13.17)

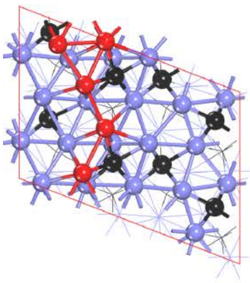

a10 (–13.09)


a11 (–13.07)

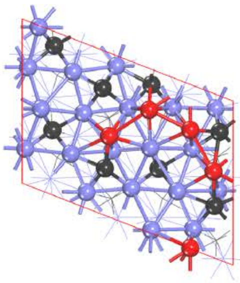

d1 (–13.88)


d2 (–13.75)

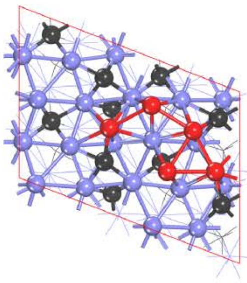
Cu5



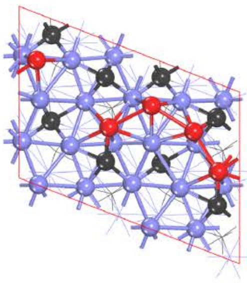
a1 (–17.09)



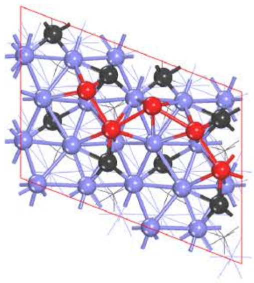
a2 (–16.97)



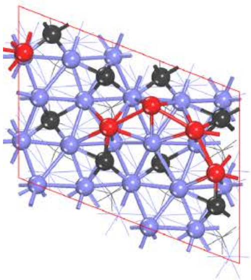
a3 (–16.97)



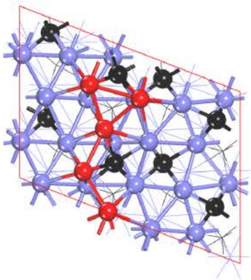
a4 (–16.90)



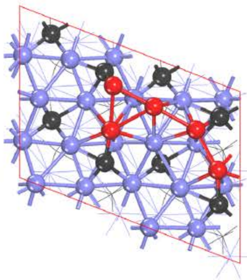
a5 (–16.89)



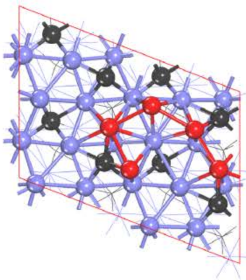
a6 (–16.86)



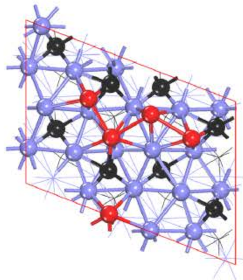
a7 (–16.85)



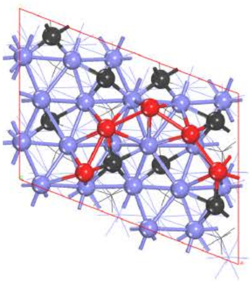
a8 (–16.85)



a9 (–16.82)



a10 (–16.79)



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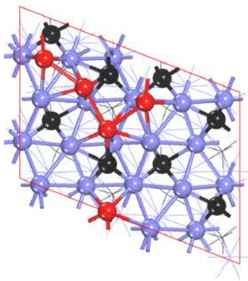
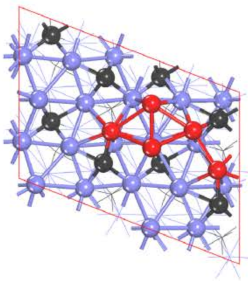
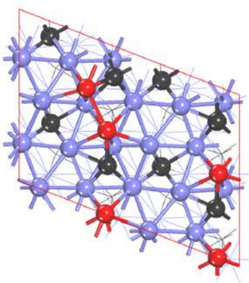


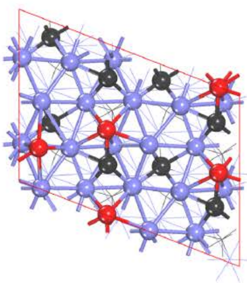
a12 (–16.71)



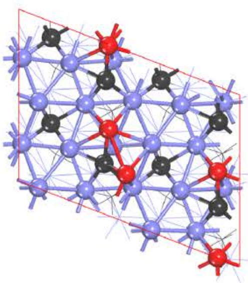
a13 (–16.71)



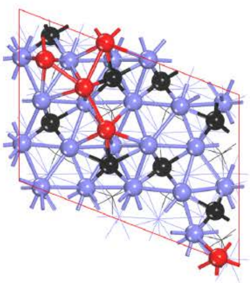
d1 (–17.20)



d2 (–17.16)

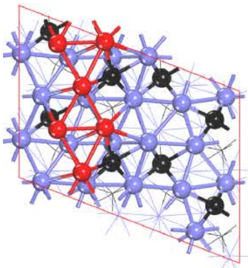


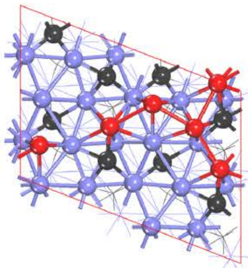
d3 (–17.12)



d4 (–17.09)

Cu6


a1 (–20.53)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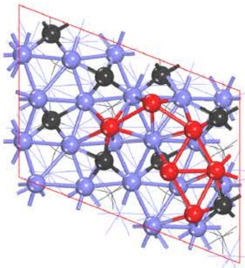
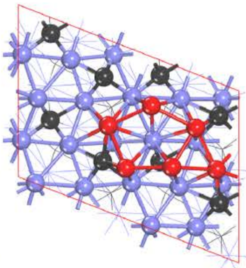

a3 (–20.46)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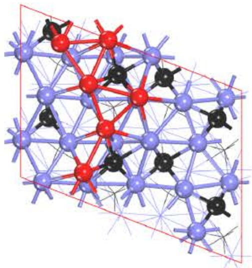
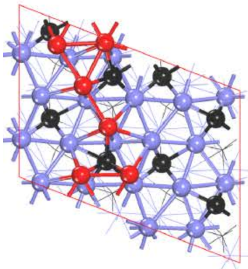
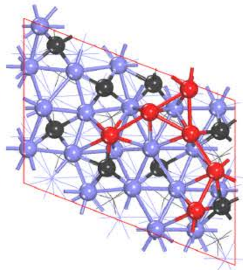
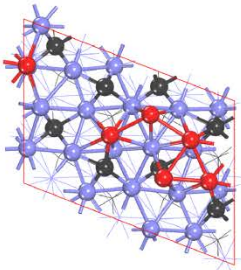
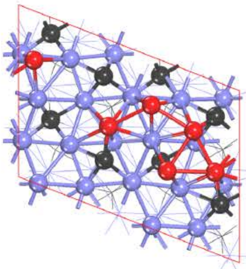
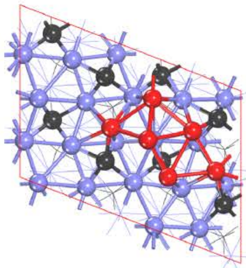

a5 (–20.32)

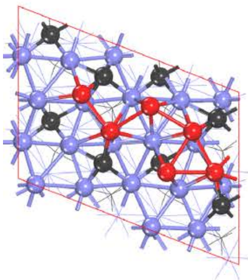

a6 (–20.29)


a7 (–20.22)


a8 (–20.21)


a9 (–20.21)


a10 (–20.18)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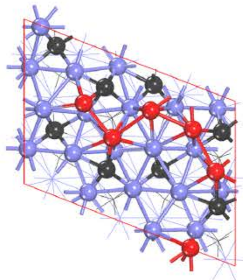
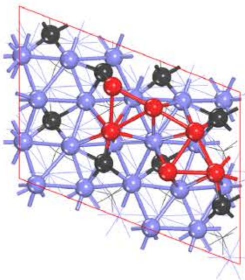

a12 (–20.13)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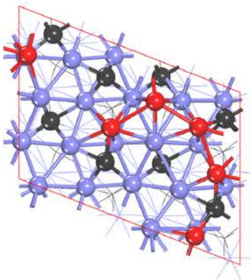
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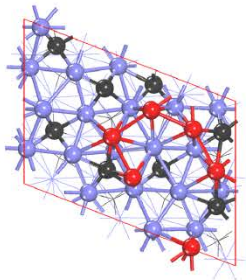
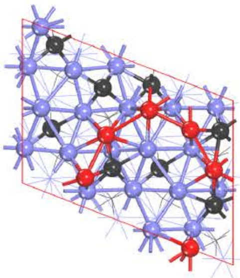
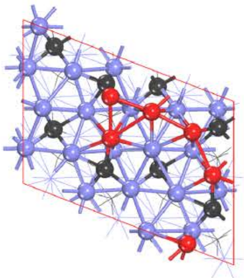
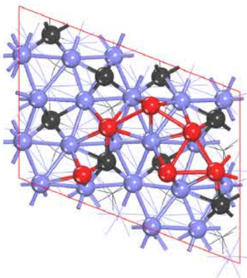

a15 (–20.07)


a16 (–19.99)


a17 (–19.96)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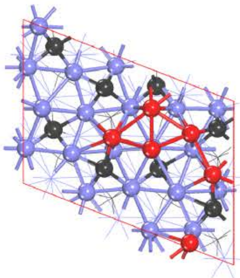
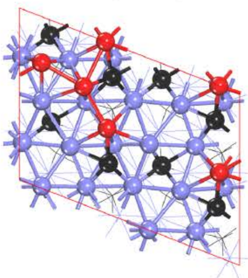

a19 (–19.88)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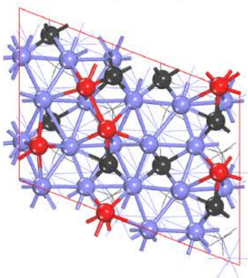
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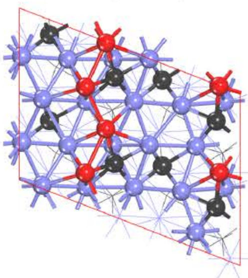
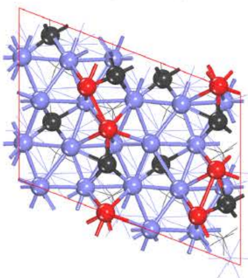
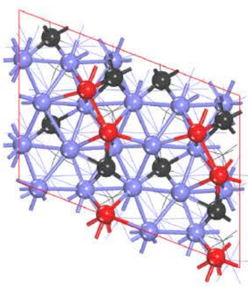
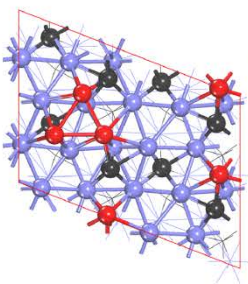

d3 (–20.49)


d4 (–20.48)


d5 (–20.46)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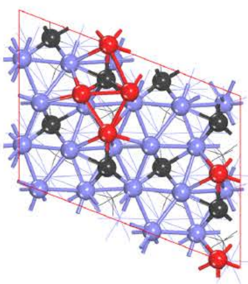
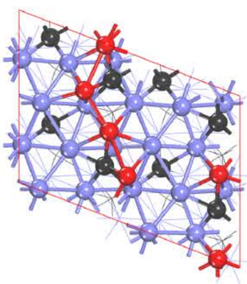
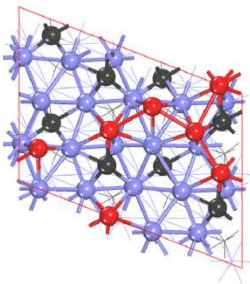
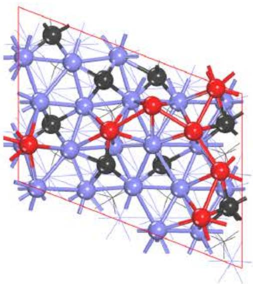
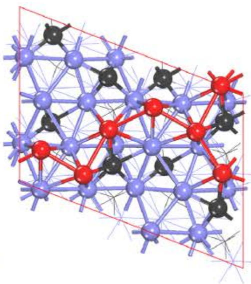

d7 (–20.38)


d8 (–20.36)

Cu7


a1 (–23.97)


a2 (–23.92)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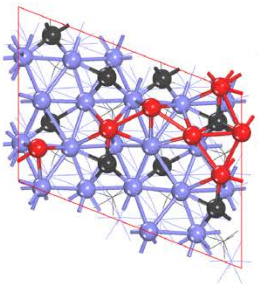
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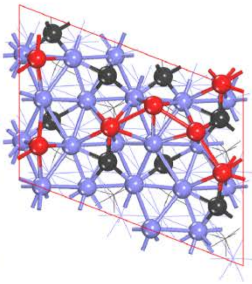
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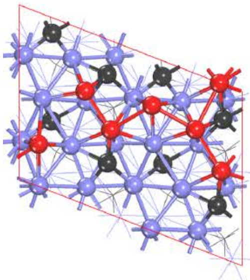
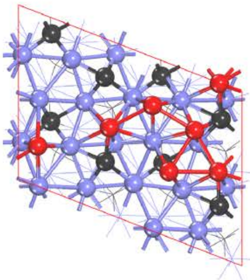

a6 (–23.76)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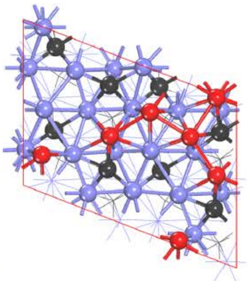
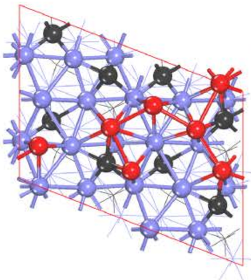
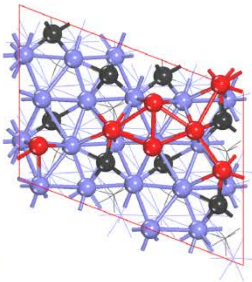
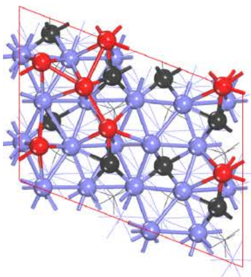
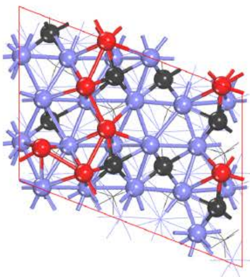
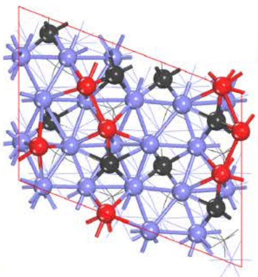

a8 (–23.67)

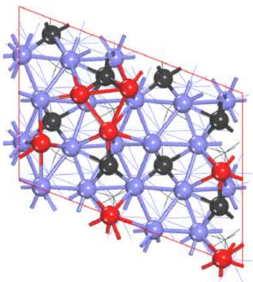

a9 (–23.62)

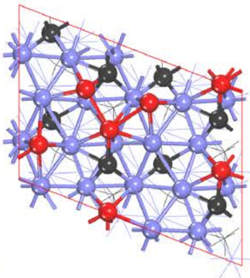

a10 (–23.51)

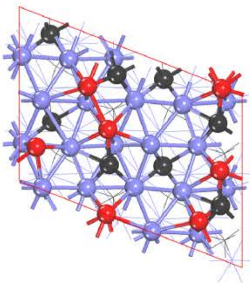

d1 (–24.13)

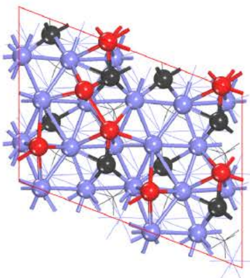

d2 (–24.07)

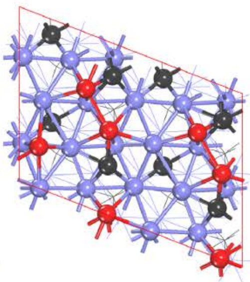

d3 (–23.83)

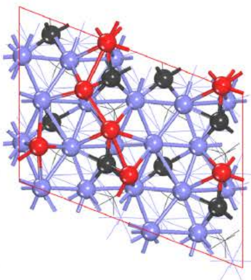

d4 (–23.76)


d5 (–23.75)

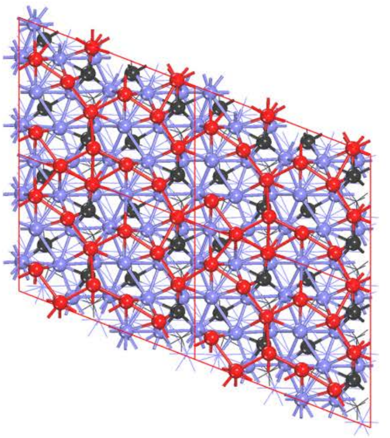

d6 (–23.75)


d7 (–23.71)

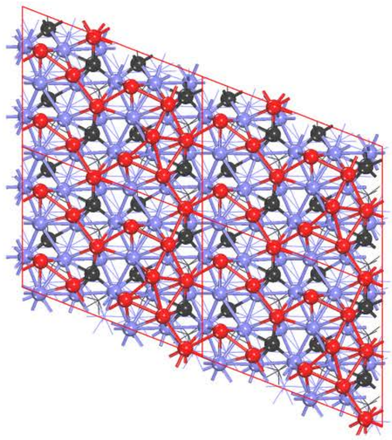

d8 (–23.69)


d9 (–23.67)

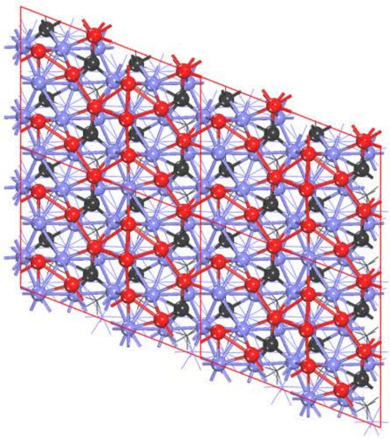
Cu13-19



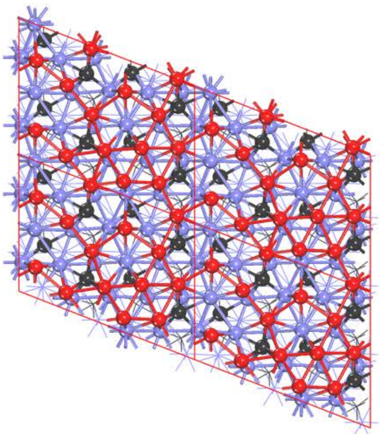
Cu13-1 (–44.87 / –3.45)



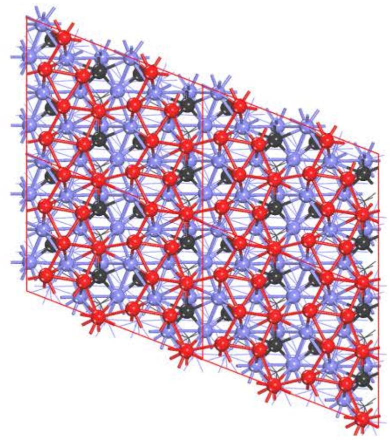
Cu13-2 (–44.83 / –3.45)



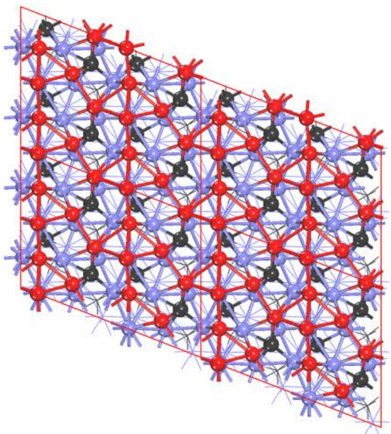
Cu13-3 (–44.82 / –3.45)



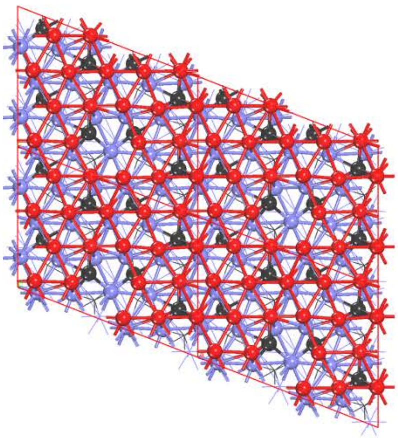
Cu14 (–48.71 / –3.48)



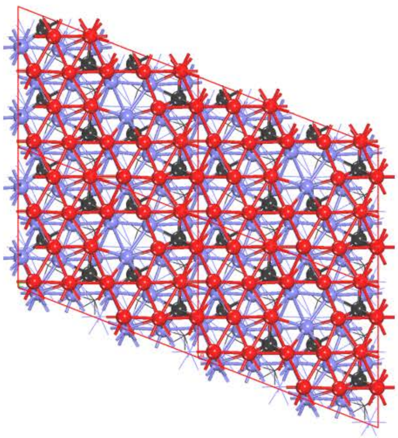
Cu16-1 (–54.99 / –3.44)



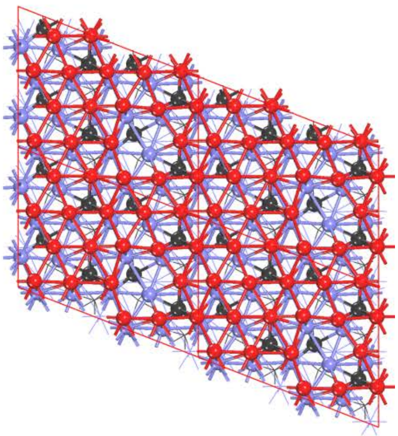
Cu16-2 (–54.98 / –3.44)



Cu19-1 (–67.29 / –3.54)

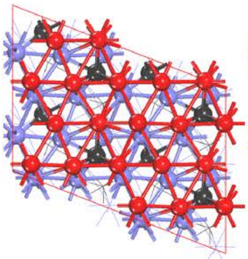


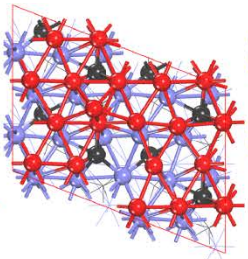
Cu19-2 (–67.22 / –3.54)

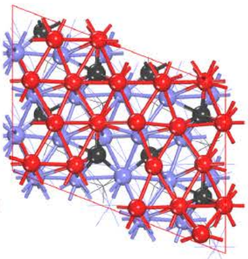


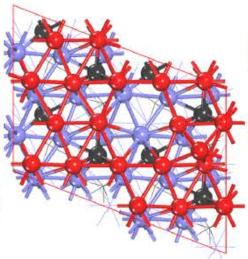
Cu19-3 (–67.16 / –3.53)

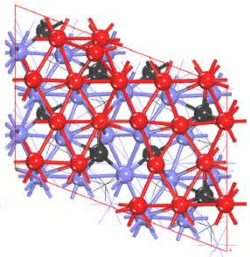
Cu20

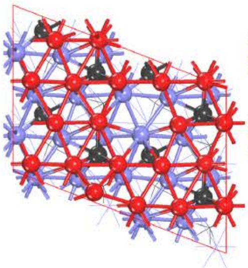

1 (–71.21)

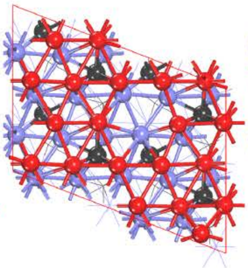

2 (–70.51)

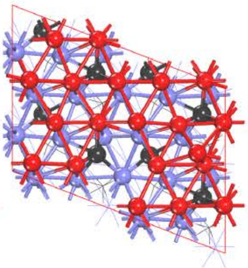

3 (–70.44)

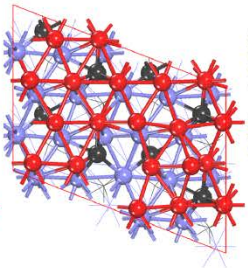

4 (–70.40)

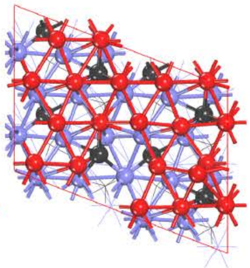

5 (–70.40)

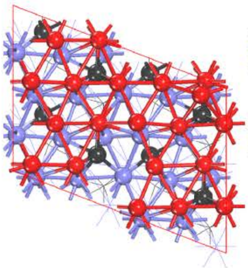

6 (–70.38)

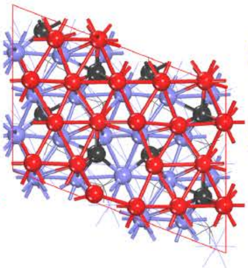

7 (–70.37)

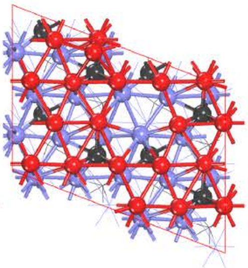

8 (–70.36)

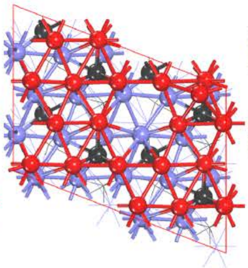

9 (–70.35)

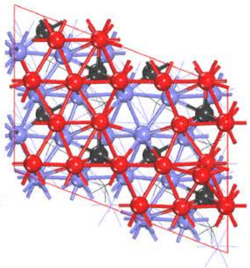

10 (–70.32)

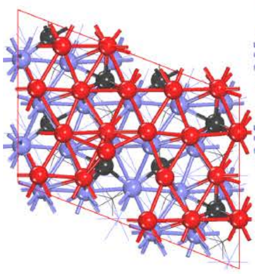

11 (–70.31)


12 (–70.29)


13 (–70.28)


14 (–70.27)


15 (–70.27)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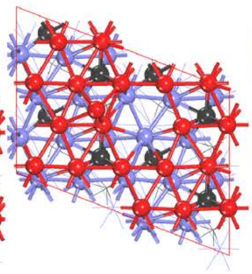
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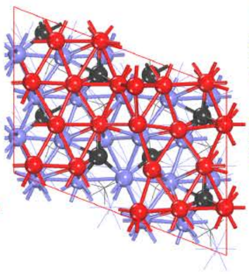
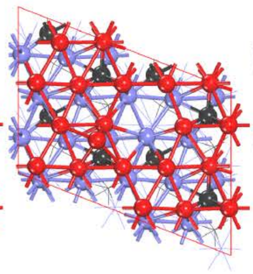

18 (–70.10)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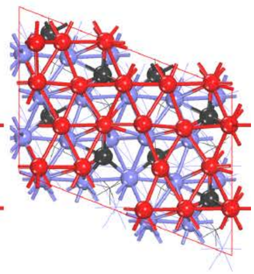
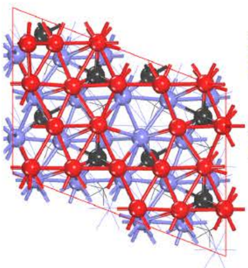
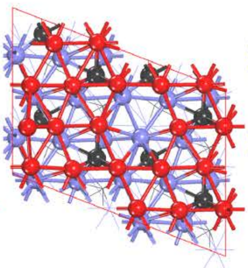
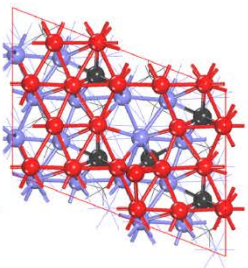
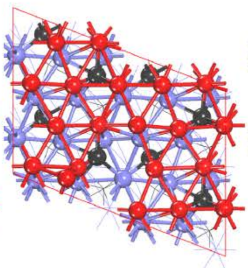
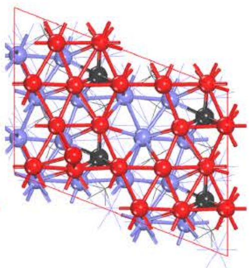

20 (–70.05)

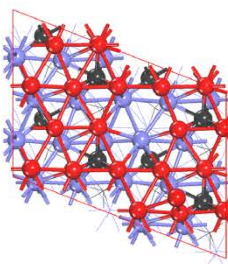

21 (–70.31)

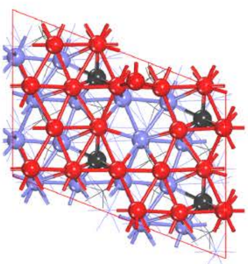

22 (–70.29)


23 (–70.28)


24 (–70.27)


25 (–70.27)


26 (–70.31)


27 (–70.29)

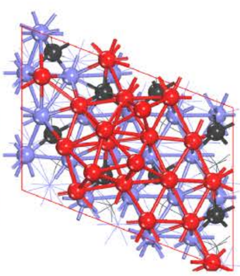

28 (–70.28)

Figure S10. Diffusion pathways of single Cu atom on the Fe_5C_2(001) surface

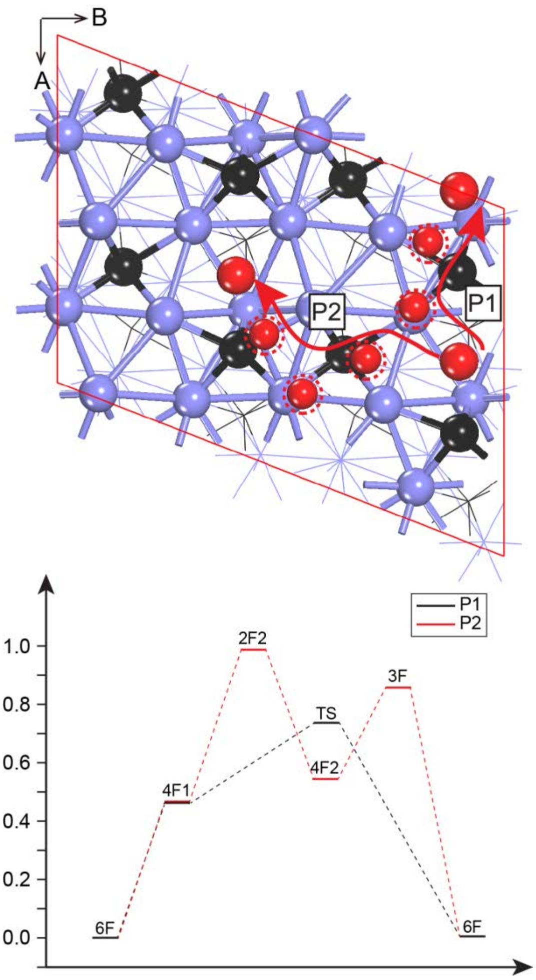


Figure S11. The top and side views of the Cu(111) and Cu_n (1 ML) on the five Fe_5C_2 surfaces.