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Supplemental information

Spectroscopic fingerprints of iron-coordinated cobalt and iron porphyrin layers on graphene

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Supplemental information

	CoTPyP		CoTPyPFe		FeTPyP		FeTPyPFe	
	Value	σ	Value	σ	Value	σ	Value	σ
Γ_1	0.27		0.27		0.27		0.27	
G_1	0.74	0.01	0.67	0.03	0.61	0.02	0.74	0.04
I_1	0.79	0.01	0.53	0.01	0.53	0.003	0.34	0.02
BE_1	398.82	0.002	399.03	0.01	398.48	0.01	398.95	0.02
Γ_2	0.27		0.27		0.27		0.27	
G_2	0.74	0.01	0.67	0.03	0.61	0.02	0.74	0.04
I_2	0.79	0.01	0.53	0.01	0.53	0.003	0.34	0.02
BE_2	399.10		399.43	0.02	398.94	0.01	399.49	0.02
Γ_3	0.27		0.27		0.27		0.27	
G_3	2.10		2.10		1.34		1.34	0.14
I_3	0.21	0.01	0.53	0.02	0.06	0.01	0.30	0.04
BE_3	400.31	0.08	400.28	0.04	399.96		400.43	0.07

Table S1: Best fit parameters of the XPS N 1*s* core level (related to Fig. 2). Γ: Lorentzian width (eV); G: Gaussian width (eV); A: Amplitude (arb. units); BE: Binding Energy (eV). Asymmetry is always set to zero. When the standard deviation (σ) is missing, it means that the parameter has been locked to a specific value. Subscripts 1 and 2 refer to iminic and pyridinic N species, respectively, and 3 to non-adiabatic features.

	CoTPyP	CoTPyPFe
FWHM	1.8	2.3
A_1	0.33	0.48
BE_1	780.1	780.7
FWHM	2.9	2.3
A_2	0.3	0.36
BE_2	782.2	782.8
FWHM	1.8	2.3
A_{GS}	0.15	0.13
BE_{GS}	778.9	778.9

Table S2: Best fit parameters of the Co 2*p*$_{3/2}$ core level for CoTPyP and CoTPyPFe (related to Fig. 3A). FWHM: Full Width Half Maximum (eV), A: Amplitude (arb. units), BE: Binding Energy (eV). Asymmetry is always set to zero. Numerical subscripts account for the multiplet splitting and shake up, and GS refers to the Gunnarsson and Schönhammer resonance. The error on binding energy is about 50 meV, and on FWHM and amplitudes is about 10% of the value.

	FeTPyP	CoTPyPFe
FWHM	1.2	4.1
A_1	0.3	0.39
BE_1	709.0	711.4
FWHM	1.2	2.3
A_2	0.16	0.85
BE_2	710.1	714.3
FWHM	2.7	
A_3	0.012	
BE_3	712.4	
FWHM	1.2	2.7
A_{GS}	0.19	0.073
BE_{GS}	707.9	708.2

Table S3: Best fit parameters of the Fe 2*p*$_{3/2}$ core level for FeTpyP and CoTPyPFe (related to Fig. 3B). FWHM: Full Width Half Maximum (eV), A: Amplitude (arb. units), BE: Binding Energy (eV). Asymmetry is always set to zero. Numerical subscripts account for the multiplet splitting and shake up, and *GS* refers to the Gunnarsson and Schönhammer resonance. Error on binding energy is about 50 meV, on Gaussian widths and amplitudes is about 10% of the value.

	300 K		470 K		550 K		650 K		970 K	
	Value	σ	Value	σ	Value	σ	Value	σ	Value	σ
Γ_1	0.27		0.27		0.27		0.27		0.27	
G_1	0.73	0.07	0.73	0.06	0.72	0.05	0.71	0.30	0.71	0.30
I_1	0.83	0.02	0.79	0.02	0.73	0.02	0.08	0.01	0.01	0.02
BE_1	398.67	0.06	398.80	0.03	398.76	0.03	398.93	0.11	398.82	
Γ_2	0.27		0.27		0.27		0.27		0.27	
G_2	0.73	0.07	0.73	0.06	0.72	0.05	0.71	0.30	0.71	0.30
I_2	0.83	0.02	0.79	0.02	0.73	0.02	0.08	0.01	0.01	0.02
BE_2	398.90	0.12	399.11	0.07	399.13	0.05	399.31	0.23	399.20	0.23
Γ_3	0.27		0.27		0.27		0.27		0.27	
G_3	2.10		2.10		2.10		2.10		2.10	
I_3	0.36	0.02	0.30	0.02	0.34	0.02	0.05	0.02	0.13	0.02
BE_3	399.82	0.09	399.95	0.09	399.95	0.09	400.07	0.09	399.97	0.09
Γ_4	0.27		0.27		0.27		0.27		0.27	
G_4	1.67	0.18	1.67	0.18	1.67	0.18	1.67	0.18	1.67	0.18
I_4	0.00		0.00		0.00		0.03	0.01	0.01	0.01
BE_4	402.02	0.06	402.15	0.06	402.15	0.06	402.28	0.06	402.17	0.06
Γ_5	0.27		0.27		0.27		0.27		0.27	
G_5	1.03	0.14	1.03	0.14	1.03	0.14	1.03	0.14	1.03	0.14
I_5	0.00	0.03	0.00	0.03	0.00	0.03	0.00	0.02	0.25	0.05
BE_5	398.27	0.07	398.40	0.07	398.36	0.07	398.53	0.07	398.40	0.07

Table S4: Best fit parameters of N 1*s* core level spectra of the CoTPyP/Gr/Ir(111) stepwise annealing experiment (related to Fig. 4A). Γ: Lorentzian width (eV); G: Gaussian width (eV); A: Amplitude (arb. units); BE: Binding Energy (eV). Asymmetry is always set to zero. When the standard deviation (σ) is missing, the parameter has been locked to a specific value. Subscripts 1 and 2 refer to iminic and pyridinic N species, respectively, 3 to non-adiabatic shakeup, 4 to graphitic N, and 5 to N atoms strongly interacting with substrate.

	300 K		550 K		600 K		650 K		700 K		970 K	
	Value	σ	Value	σ	Value	σ	Value	σ	Value	σ	Value	σ
Γ_1	0.27		0.27		0.27		0.27		0.27		0.27	
G_1	0.60	0.02	0.61	0.03	0.64	0.05	0.71	0.16	0.71	0.16	0.71	0.16
I_1	0.53	0.01	0.45	0.01	0.27	0.01	0.07	0.01	0.05	0.01	0.00	0.01
BE_1	398.50	0.01	398.62	0.01	398.58	0.02	398.70	0.06	398.70	0.06	398.70	0.06
Γ_2	0.27		0.27		0.27		0.27		0.27		0.27	
G_2	0.60	0.02	0.61	0.03	0.64	0.05	0.71	0.16	0.71	0.16	0.71	0.16
I_2	0.53	0.01	0.45	0.01	0.27	0.01	0.07	0.01	0.05	0.01	0.00	0.01
BE_2	398.96	0.01	399.06	0.01	399.06	0.02	399.18	0.02	399.18	0.02	399.18	0.02
Γ_3	0.27		0.27		0.27		0.27		0.27		0.27	
G_3	1.34		1.34		1.34		1.34		1.34		1.34	
I_3	0.05	0.01	0.13	0.01	0.04	0.01	0.00	0.01	0.01	0.01	0.01	0.01
BE_3	399.98		400.10		400.06		400.18		400.18		400.18	
Γ_4	0.27		0.27		0.27		0.27		0.27		0.27	
G_4	1.00	0.39	1.00	0.39	1.00	0.39	1.00	0.39	1.00	0.39	1.00	0.39
I_4	0.00	0.02	0.00	0.02	0.00	0.02	0.00	0.02	0.04	0.03	0.04	0.03
BE_4	398.20	0.26	398.32	0.26	398.28	0.26	398.40	0.26	398.40	0.26	398.40	0.26

Table S5: Best fit parameters of N 1*s* core level spectra of the FeTPyP/Gr/Ir(111) stepwise annealing experiment (related to Fig. 4B). Γ: Lorentzian width (eV); G: Gaussian width (eV); A: Amplitude (arb. units); BE: Binding Energy (eV). Asymmetry is always set to zero. When the standard deviation (σ) is missing, the parameter has been locked to a specific value. Subscripts 1 and 2 refer to iminic and pyridinic N species, respectively, 3 to non-adiabatic shakeup, and 4 to N atoms strongly interacting with substrate.

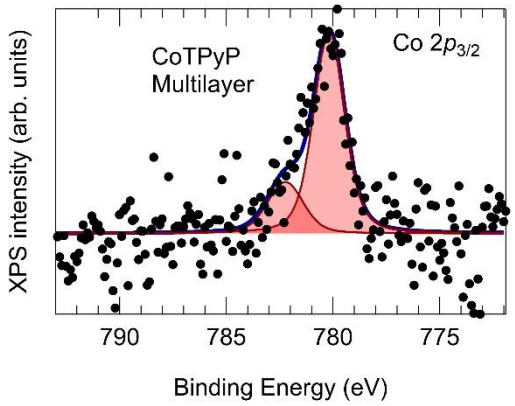

Figure S1: Co 2$p_{3/2}$ core level spectrum for the CoTPyP multilayer. Experimental data (dotted curves) are plotted together with its best fit function (solid line) and deconvolution (filled profiles)..

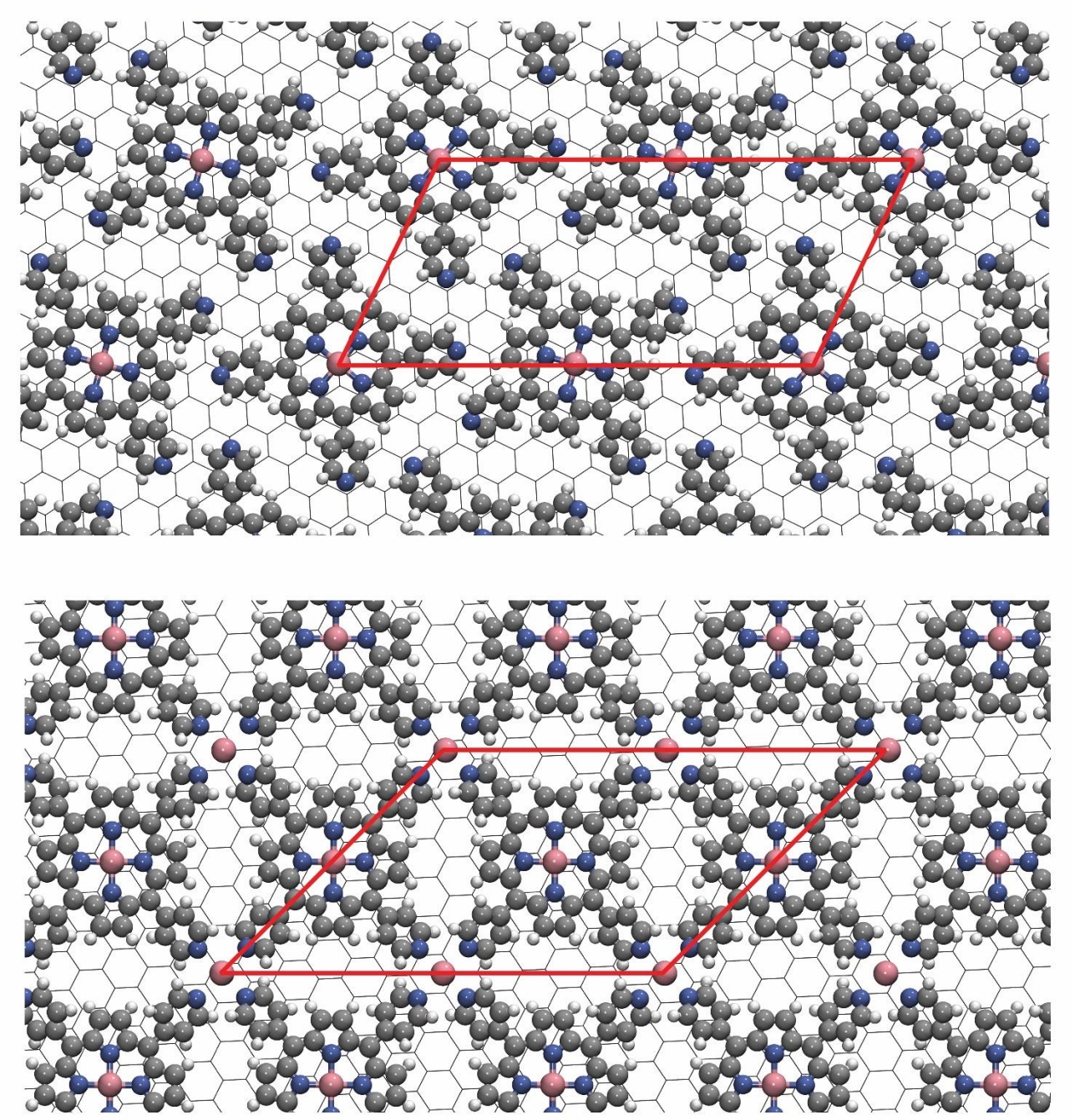

Figure S2. Top views of the computationally optimized structures for the mono- (top) and bi-metallic (bottom) layers on graphene. The unit cells are also depicted (red lines). Color codes: c (gray), N (blue), H (white), and metal (pink).