Supporting Information

Calculated relative energies for selected states of FeP, FeP(Im), and FeP(Im)(O_2) at different functionals' optimized structures and with different basis sets. Calculated relative energies for selected states of FeP, FeP(Im) and FeP(Im)(O_2) with various recently developed functionals. Calculated FeP–Im bonding energies in FeP(Im) and FeP(Im)–O_2 bonding energies in FeP(Im)(O_2) with various functionals in the non-SCF and SCF procedures. Non-relativistic relative energies for selected states of FeP, FeP(Im), and FeP(Im)(O_2).

Table S1. Calculated relative energies ($E^{relative}$, eV) for the intermediate- (S = 1)[a], high- (S = 2), and low-spin (S = 0) states of FeP at different functionals' optimized structures

		S = 2				S = 0			
		BP-Struct	OLYP-Struct	B3LYP-Struct	PBE0-Struct	BP-Struct	OLYP-Struct	B3LYP-Struct	PBE0-Struct
GGA	BP	0.69	0.69	0.69	0.70	1.48	1.49	1.51	1.49
	PBE	0.69	0.68	0.68	0.70	1.48	1.49	1.51	1.49
	revPBE	0.55	0.54	0.55	0.56	1.43	1.44	1.45	1.43
	OPBE	0.19	0.18	0.19	0.21	1.39	1.40	1.43	1.40
	OPerdew	0.20	0.19	0.20	0.21	1.45	1.46	1.49	1.46
	OLYP	0.24	0.23	0.24	0.25	1.40	1.41	1.42	1.39
	HCTH/407	0.03	0.02	0.03	0.04	1.57	1.59	1.60	1.57
Meta-GGA	Becke00	0.34	0.32	0.33	0.34	1.50	1.52	1.51	1.49
	τ-HCTH	0.07	0.07	0.07	0.08	1.50	1.51	1.54	1.51
Hybrid-GGA	B3LYP	0.19	0.19	0.19	0.19	1.50	1.51	1.51	1.48
	B3LYP*	0.35	0.35	0.35	0.35	1.49	1.50	1.50	1.48
	O3LYP	-0.01	0.00	-0.01	0.00	1.44	1.46	1.48	1.45
	PBE0	-0.01	-0.01	-0.02	-0.01	1.56	1.57	1.58	1.55
	B97	0.09	0.09	0.09	0.09	1.41	1.44	1.43	1.40
	τ-HCTH-hyb	0.21	0.21	0.21	0.21	1.46	1.47	1.48	1.46

[a]The relative energy for the S = 1 state is set to zero.

Table S2. Calculated relative energies ($E^{relative}$, eV) for the intermediate- (S = 1)[a], high- (S = 2), and low-spin (S = 0) states of FeP with different basis sets

		S = 2				S = 0			
		DZP	TZP	TZ2P	TZ2P+	DZP	TZP	TZ2P	TZ2P+
GGA	BP	0.72	0.69	0.70	0.70	1.40	1.48	1.50	1.49
	PBE	0.75	0.69	0.70	0.70	1.40	1.48	1.49	1.49
	revPBE	0.62	0.55	0.56	0.55	1.34	1.43	1.44	1.43
	OPBE	0.28	0.19	0.21	0.21	1.30	1.39	1.39	1.39
	OPerdew	0.28	0.20	0.22	0.22	1.36	1.45	1.45	1.45
	OLYP	0.30	0.24	0.25	0.25	1.30	1.40	1.40	1.39
	HCTH/407	0.14	0.03	0.05	0.04	1.47	1.57	1.58	1.57
Meta-GGA	Becke00	0.34	0.34	0.30	0.29	1.39	1.50	1.43	1.42
	τ-HCTH	0.10	0.07	0.09	0.09	1.42	1.50	1.50	1.50
Hybrid-GGA	B3LYP	0.22	0.19	0.21	0.20	1.41	1.50	1.52	1.51
	B3LYP*	0.38	0.35	0.36	0.36	1.40	1.49	1.51	1.50
	O3LYP	0.07	-0.01	0.03	0.03	1.36	1.44	1.46	1.46
	PBE0	0.05	-0.01	0.01	0.00	1.47	1.56	1.58	1.57
	B97	0.16	0.09	0.10	0.10	1.33	1.41	1.42	1.42
	τ-HCTH-hyb	0.28	0.21	0.23	0.22	1.37	1.46	1.47	1.46

[a]The relative energy for the S = 1 state is set to zero.

Table S3. Calculated relative energies ($E^{relative}$, eV) for the intermediate- (S = 1)[a], high- (S = 2), and low-spin (S = 0) states of FeP(Im) at different functionals' optimized structures

		S = 2				S = 0			
		BP-Struct	OLYP-Struct	B3LYP-Struct	PBE0-Struct	BP-Struct	OLYP-Struct	B3LYP-Struct	PBE0-Struct
GGA	BP	0.49	0.48	0.49	0.49	-0.02	-0.04	0.02	0.01
	PBE	0.44	0.45	0.45	0.45	-0.10	-0.10	-0.02	-0.03
	revPBE	0.30	0.32	0.32	0.31	0.02	0.04	0.10	0.09
	OPBE	-0.02	0.01	-0.01	-0.01	0.14	0.17	0.27	0.23
	OPerdew	-0.01	0.01	0.00	-0.01	0.14	0.17	0.26	0.22
	OLYP	0.01	0.04	0.03	0.02	0.18	0.22	0.27	0.24
	HCTH/407	-0.20	-0.16	-0.18	-0.18	0.26	0.31	0.38	0.35
Meta-GGA	Becke00	-0.05	-0.03	-0.02	-0.04	0.11	0.12	0.13	0.11
	τ-HCTH	-0.14	-0.12	-0.13	-0.14	0.27	0.28	0.27	0.25
Hybrid-GGA	B3LYP	-0.10	-0.08	-0.08	-0.09	0.40	0.39	0.38	0.37
	B3LYP*	0.07	0.08	0.08	0.08	0.26	0.25	0.26	0.25
	PBE0	-0.29	-0.28	-0.28	-0.28	0.46	0.45	0.50	0.48
	B97	-0.20	-0.18	-0.18	-0.19	0.32	0.32	0.39	0.37
	τ-HCTH-hyb	-0.07	-0.05	-0.05	-0.06	0.20	0.18	0.26	0.25

[a]The relative energy for the S = 1 state is set to zero.

Table S4. Calculated relative energies ($E^{relative}$, eV) for the intermediate- (S = 1)[a], high- (S = 2), and low-spin (S = 0) states of FeP(Im) with different basis sets

		S = 2				S = 0			
		DZP	TZP	TZ2P	TZ2P+	DZP	TZP	TZ2P	TZ2P+
GGA	BP	0.54	0.49	0.50	0.50	-0.07	-0.02	-0.03	-0.03
	PBE	0.49	0.44	0.45	0.46	-0.15	-0.10	-0.10	-0.11
	revPBE	0.36	0.30	0.31	0.32	-0.03	0.02	0.02	0.01
	OPBE	0.06	-0.02	0.00	0.01	0.05	0.14	0.13	0.12
	OPerdew	0.06	-0.01	0.01	0.02	0.06	0.14	0.13	0.12
	OLYP	0.07	0.01	0.03	0.03	0.12	0.18	0.18	0.17
	HCTH/407	-0.14	-0.20	-0.18	-0.18	0.21	0.26	0.25	0.25
Meta-GGA	Becke00	0.01	-0.05	-0.04	-0.03	0.06	0.11	0.10	0.10
	τ-HCTH	-0.07	-0.14	-0.13	-0.13	0.21	0.27	0.26	0.26
Hybrid-GGA	B3LYP	-0.05	-0.10	-0.09	-0.09	0.34	0.40	0.39	0.39
	B3LYP*	0.12	0.07	0.08	0.08	0.21	0.26	0.25	0.25
	PBE0	-0.23	-0.29	-0.28	-0.28	0.38	0.46	0.46	0.45
	B97	-0.14	-0.20	-0.19	-0.18	0.25	0.32	0.31	0.30
	τ-HCTH-hyb	-0.01	-0.07	-0.06	-0.05	0.14	0.20	0.20	0.19

[a]The relative energy for the S = 1 state is set to zero.

Table S5. Calculated relative energies ($E^{relative}$, eV) for the closed-shell (S = 0)[a], triplet- (S = 1), and low-spin (S = 0), open-shell states of FeP(Im)(O_2) at different functionals' optimized structures

		S = 1				S = 0 (open shell singlet)			
		BP-Struct	OLYP-Struct	B3LYP-Struct	PBE0-Struct	BP-Struct	OLYP-Struct	B3LYP-Struct	PBE0-Struct
GGA	BP	0.01	0.01	0.02	0.19	0.20	0.31	0.31	0.45
	PBE	0.03	0.03	0.09	0.22	0.21	0.45	0.42	0.53
	revPBE	0.00	0.00	0.09	0.23	0.18	0.30	0.36	0.45
	OPBE	0.01	0.03	0.03	0.10	0.26	0.26	0.25	0.31
	OPerdew	0.01	0.03	0.04	0.12	0.26	0.28	0.26	0.33
	OLYP	-0.01	0.00	0.04	0.13	0.23	0.17	0.21	0.26
	HCTH/407	-0.06	-0.05	-0.04	-0.04	0.20	0.09	0.07	0.06
Meta-GGA	Becke00	-0.19	-0.20	-0.09	0.02	0.06	0.06	0.15	0.20
	τ-HCTH	-0.05	-0.03	-0.03	0.02	0.22	0.07	0.03	0.08
Hybrid-GGA	B3LYP	-0.42	-0.44	-0.39	-0.35	-0.17	-0.38	-0.39	-0.34
	B3LYP*	-0.30	-0.32	-0.26	-0.20	-0.07	-0.16	-0.18	-0.11
	PBE0	-0.51	-0.53	-0.51	-0.49	-0.25	-0.47	-0.52	-0.48
	B97	-0.37	-0.39	-0.33	-0.27	-0.12	-0.26	-0.23	-0.18
	τ-HCTH-hyb	-0.32	-0.34	-0.29	-0.23	-0.07	-0.12	-0.12	-0.06

[a]The relative energy for the closed-shell singlet is set to zero.

Table S6. Calculated relative energies ($E^{relative}$, eV) for the closed-shell (S = 0)[a], triplet- (S = 1), and low-spin (S = 0), open-shell states of FeP(Im)(O_2) with different basis sets

		S = 1				S = 0 (open shell singlet)			
		DZP	TZP	TZ2P	TZ2P+	DZP	TZP	TZ2P	TZ2P+
GGA	BP	0.01	0.01	0.01	0.00	0.20	0.20	0.20	0.20
	PBE	0.02	0.03	0.02	0.02	0.21	0.21	0.21	0.20
	revPBE	0.00	0.00	0.00	-0.01	0.18	0.18	0.18	0.17
	OPBE	0.01	0.01	0.00	0.00	0.27	0.26	0.26	0.25
	OPerdew	0.01	0.01	0.01	0.00	0.27	0.26	0.26	0.25
	OLYP	-0.01	-0.01	-0.01	-0.02	0.24	0.23	0.23	0.23
	HCTH/407	-0.07	-0.06	-0.06	-0.07	0.21	0.20	0.20	0.19
Meta-GGA	Becke00	-0.20	-0.19	-0.21	-0.22	0.06	0.06	0.03	0.02
	τ-HCTH	-0.05	-0.05	-0.05	-0.06	0.24	0.22	0.22	0.22
Hybrid-GGA	B3LYP	-0.45	-0.42	-0.42	-0.43	-0.18	-0.17	-0.19	-0.19
	B3LYP*	-0.33	-0.30	-0.31	-0.31	-0.07	-0.07	-0.08	-0.08
	PBE0	-0.54	-0.51	-0.52	-0.52	-0.25	-0.25	-0.26	-0.27
	B97	-0.40	-0.37	-0.38	-0.38	-0.12	-0.12	-0.13	-0.13
	τ-HCTH-hyb	-0.35	-0.32	-0.33	-0.33	-0.06	-0.07	-0.08	-0.08

[a]The relative energy for the closed-shell singlet is set to zero.

Table S7. Calculated relative energies ($E^{relative}$ in eV) for selected states of FeP, FeP(Im) and FeP(Im)(O_2) with various recently developed functionals

		FeP			FeP(Im)			FeP(Im)(O_2)		
		S = 1	S = 2	S = 0	S = 1	S = 2	S = 0	S = 0 (C)[a]	S = 1	S = 0 (O)[b]
GGA	PBEsol[c]	0	0.80	1.48	0	0.62	-0.19	0	0.08	0.31
	RGE2[d]	0	0.65	1.44	0	0.47	-0.06	0	0.05	0.28
	SSB-D[e]	0	0.12	1.59	0	-0.03	0.22	0	-0.07	0.17
Meta-GGA	M06-L[f]	0	0.04	1.16	0	-0.09	0.20	0	-0.15	0.15
	TPSS[g]	0	0.75	1.38	0	0.48	-0.08	0	-0.06	0.13
	revTPSS[h]	0	0.71	1.46	0	0.43	-0.08	0	-0.04	0.14
Hybrid-GGA	M05[i]	0	-0.51	1.37	0	-0.48	0.75	0	-0.35	0.01
	M05-2x[j]	0	-0.74	1.90	0	-0.99	1.17	0	-1.00	-0.65
	M06[k]	0	-0.33	1.36	0	-0.28	0.58	0	-0.36	-0.01
	M06-2x[l]	0	-0.89	1.72	0	-1.04	1.20	0	-1.06	-0.60
	TPSSh[m]	0	0.46	1.42	0	0.19	0.14	0	-0.26	-0.05

[a]Closed-shell singlet.

[b]Open-shell singlet.

[c]PBEsol: Revised PBE functional for solids, proposed in 2008 by Perdew et al. (Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X.; Burke, K. *Phys. Rev. Lett.* **2008**, *100*, 136406).

[d]RGE2: Regularized gradient expansion (RGE) approximation density functional proposed in 2009 by Ruzsinszky, Csonka, and Scuseria (Ruzsinszky, A.; Csonka, G. I.; Scuseria, G. E. *J. Chem. Theory Comput.* **2009**, *5*, 763).

[e]SSB-D: Empirical GGA functional including a dispersion correction, proposed in 2009 by Swart, Sola, and Bickelhaupt (Swart, M.; Sola, M.; Bickelhaupt, F. M. *J. Chem. Phys.* **2009**, *131*, 094103).

[f]M06-L: Zhao-Truhlar's (2006) meta-GGA functional (Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101).

[g]TPSS: Tao-Perdew-Staroverov-Scuseria's (2003) nonempirical meta-GGA functional (Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401).

[h]revTPSS: Revised TPSS functional proposed in 2009 by Perdew et al. (Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Constantin, L. A.; Sun, J. *Phys. Rev. Lett.* **2009**, *103*, 026403).

[i]M05: Zhao-Schultz-Truhlar's (2005) hybrid meta-GGA functional that contains 28% Hartree-Fock exchange (Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Phys.* **2005**, *123*, 161103).

[j]M05-2X: The Hartree-Fock exchange admixture is increased (doubled) from 28% in original M05 to 56% (Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory Comput.* **2006**, *2*, 364).

[k]M06: Zhao-Truhlar's (2006) hybrid meta-GGA functional that contains 27% Hartree-Fock exchange (Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215).

[l]M06-2X: The Hartree-Fock exchange admixture is increased (doubled) from 27% in original M06 to 54% (Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.* **2008**, *120*, 215).

[m]TPSSh: A one-parameter global hybrid version of the TPSS functional (Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119*, 12129).

Table S8. Calculated FeP–Im bonding energies in FeP(Im) and FeP(Im)–O_2 bonding energies in FeP(Im)(O_2) with various functionals in the non-SCF and SCF procedures (E_{bond} in eV)

		E_{bond}(FeP–Im)		E_{bond}[Fe(Im)–O_2]	
		non-SCF	SCF	non-SCF	SCF
GGA	PBE	0.63	0.66	0.89	0.88
	revPBE	0.37	0.38	0.51	0.50
	OPBE	0.33	0.35	0.05	0.04
	OPerdew	0.40		0.17	
	OLYP	0.22	0.26	0.10	0.10
	HCTH/407	0.54		-0.01	
meta-GGA	Becke00	0.26		0.31	
	τ-HCTH	0.59		0.21	
Hybrid-GGA	B3LYP	0.25	0.13	-0.14	0.05
	B3LYP*	0.28	0.30	0.21	0.18
	PBE0	0.58	0.53	-0.48	-0.24
	B97	0.41		-0.27	
	τ-HCTH-hyb	0.42		0.16	
GGA	PBEsol	1.02		1.11	
	RGE2	0.69		0.84	
	SSB-D	0.92		0.53	
Meta-GGA	M06-L	0.92		0.63	
	TPSS	0.51		0.77	
	revTPSS	0.54		0.84	
Hybrid-GGA	M05	0.60		-0.92	
	M05-2x	0.50		-2.20	
	M06	0.75	0.89	-0.32	-0.33
	M06-2x	0.47	1.02	-2.34	-1.60
	TPSSh	0.35	0.26	0.41	0.44

Table S9. Non-relativistic relative energies ($E^{relative}$, eV) for the intermediate- (S = 1), high- (S = 2), and low-spin (S = 0) states of FeP

		S = 1	S = 2	S = 0
GGA	BP	0	0.66 (0.69)[a]	1.43 (1.48)[a]
	PBE	0	0.66 (0.69)	1.43 (1.48)
	revPBE	0	0.52 (0.55)	1.39 (1.43)
	OPBE	0	0.16 (0.19)	1.35 (1.39)
	OPerdew	0	0.17 (0.20)	1.41 (1.45)
	OLYP	0	0.21 (0.24)	1.36 (1.40)
	HCTH/407	0	0.00 (0.03)	1.53 (1.57)
Meta-GGA	Becke00	0	0.30 (0.34)	1.46 (1.50)
	τ-HCTH	0	0.04 (0.07)	1.46 (1.50)
Hybrid-GGA	B3LYP	0	0.15 (0.19)	1.46 (1.50)
	B3LYP*	0	0.32 (0.35)	1.45 (1.49)
	PBE0	0	-0.05 (-0.01)	1.53 (1.56)
	B97	0	0.05 (0.09)	1.38 (1.41)
	τ-HCTH-hyb	0	0.17 (0.21)	1.42 (1.46)

[a]The values in parentheses are the relativistic results for comparison.

Table S10. Non-relativistic relative energies ($E^{relative}$, eV) for the intermediate- (S = 1), high- (S = 2), and low-spin (S = 0) states of FeP(Im)

		S = 1	S = 2	S = 0
GGA	BP	0	0.45 (0.49)[a]	0.02 (-0.02)[a]
	PBE	0	0.40 (0.44)	-0.06 (-0.10)
	revPBE	0	0.26 (0.30)	0.06 (0.02)
	OPBE	0	-0.05 (-0.02)	0.17 (0.14)
	OPerdew	0	-0.05 (-0.01)	0.16 (0.14)
	OLYP	0	-0.03 (0.01)	0.22 (0.18)
	HCTH/407	0	-0.23 (-0.20)	0.30 (0.26)
Meta-GGA	Becke00	0	-0.09 (-0.05)	0.17 (0.11)
	τ-HCTH	0	-0.18 (-0.14)	0.30 (0.27)
Hybrid-GGA	B3LYP	0	-0.15 (-0.10)	0.44 (0.40)
	B3LYP*	0	0.02 (0.07)	0.30 (0.26)
	PBE0	0	-0.34 (-0.29)	0.50 (0.46)
	B97	0	-0.24 (-0.20)	0.35 (0.32)
	τ-HCTH-hyb	0	-0.11 (-0.07)	0.24 (0.20)

[a]The values in parentheses are the relativistic results for comparison.

Table S11. Non-relativistic relative energies ($E^{relative}$, eV) for the closed-shell (S = 0), triplet- (S = 1), and low-spin (S = 0), open-shell states of FeP(Im)(O_2)

		S = 0 (C)[a]	S = 1	S = 0 (O)[b]
GGA	BP	0	-0.01 (0.01)[c]	0.18 (0.20)[c]
	PBE	0	0.00 (0.03)	0.19 (0.21)
	revPBE	0	-0.02 (0.00)	0.16 (0.18)
	OPBE	0	-0.01 (0.01)	0.24 (0.26)
	OPerdew	0	-0.01 (0.01)	0.25 (0.26)
	OLYP	0	-0.03 (-0.01)	0.22 (0.23)
	HCTH/407	0	-0.08 (-0.06)	0.18 (0.20)
Meta-GGA	Becke00	0	-0.22 (-0.19)	0.02 (0.06)
	τ-HCTH	0	-0.06 (-0.05)	0.22 (0.22)
Hybrid-GGA	B3LYP	0	-0.36 (-0.42)	-0.20 (-0.17)
	B3LYP*	0	-0.33 (-0.30)	-0.09 (-0.07)
	PBE0	0	-0.53 (-0.51)	-0.27 (-0.25)
	B97	0	-0.40 (-0.37)	-0.14 (-0.12)
	τ-HCTH-hyb	0	-0.35 (-0.32)	-0.09 (-0.07)

[a]Closed-shell singlet.
[b]Open-shell singlet.
[c]The values in parentheses are the relativistic results for comparison.