Supplementary Information for: Role of metal atoms in the refractivity of cysteine- and phenylalanine-based metalorganic crystals

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S1. Density Functional Theory Calculations – Convergence Tests

In the main text, we presented density functional theory (DFT) calculations of the structural and refractive properties of bio-inspired metal (Cu, Zn) amino-acid (phenylalanine, cysteine) crystals. The computational details are given in section 2.2 of the main text. Here, we present convergence tests of the results with respect to the plane-wave kinetic energy cutoff and the reciprocal space k-grid density. All convergence tests were performed using the PBE functional.



Fig. S1. Total energy convergence tests for the Phe-Cu crystal with respect to the (a) planewave kinetic energy cutoff and (b) size of reciprocal space *k*-grid mesh.



Fig. S2. Total energy convergence tests for the Cys-Zn crystal with respect to the (a) planewave kinetic energy cutoff and (b) size of reciprocal space k-grid mesh.

As can be seen in Fig. S1 and Fig. S2, the planewave kinetic energy cutoff value of 700 eV and the k-grid density of $5 \times 5 \times 5$, used to obtain the results presented in the main text, provide total energy convergence to within 1 meV/unit cell for the Phe-Cu and Cys-Zn crystals.

S2. Structural parameters of the optimized crystal structures

Tables S1 and S2 summarize the structural parameters of all optimized crystal structures considered in this work. The optimization results are presented in Fig. 1 of the main text.

Table S1. Lattice parameters of optimized phenylalanine-based crystals (denoted "Opt" in the table), compared to the experimental structure deduced from X-ray diffraction (denoted "exp"). Δ and Δ (%) represent the difference between the calculated and experimental coordinates, in units of the specific parameter and percent.

		Unit cell	Lattice vectors (Å)			Lattice angles (°)		
		volume (ų)	a:	b:	c:	α:	β:	γ:
Phe-Cu exp		804.00	9.48	5.15	16.67	90	98.9	90
	Opt	802.36	9.63	5.06	16.75	90	100.3	90
Phe-Cu triplet	Δ	-1.64	0.15	-0.09	0.08	0	1.4	0
	Δ (%)	-0.20	1.60	-1.80	0.50	0	1.4	0
Phe-Cu open-	Opt	802.36	9.63	5.06	16.75	90	100.3	90
shell singlet	Δ	-1.64	0.15	-0.09	0.08	0	1.4	0
Shen Shigher	Δ (%)	-0.20	1.60	-1.80	0.50	0	1.4	0
Phe-7n closed	Opt	796.17	9.58	5.07	16.60	90	98.9	90
shell	Δ	-7.83	0.10	-0.08	-0.07	0	0	0
Shen	Δ (%)	-1.00	1.00)0 -1.50 -	-0.40	0	0	0
Phe-Zn open- shell singlet	Opt	796.17	9.58	5.07	16.60	90	98.9	90
	Δ	-7.83	0.10	-0.08	-0.07	0	0	0
	Δ (%)	-1.00	1.00	-1.50	-0.40	0	0	0
Phe metal-free	Opt	848.94	9.35	5.49	17.14	90	105.2	90
	Δ	44.94	-0.13	0.34	0.47	0	6.3	0
	Δ (%)	5.60	-1.40	6.70	2.80	0	6.4	0

Table S2. Lattice parameters of optimized cysteine-based crystals (denoted "Opt" in the table), compared to the experimental structure deduced from X-ray diffraction (denoted "exp") reported in Ref. ¹. Δ and Δ (%) represent the difference between the calculated and experimental coordinates, in units of the specific parameter and percent.

		Unit-cell	Lattice vectors (Å)			Lattice angles (°)		
		volume (Å ³)	a:	b:	c:	α:	β:	γ:
Cys-Zn exp		500.65	6.03	8.84	9.40	90	90	90
	Opt	515.20	6.05	8.84	9.64	90	90	90
Cys-Cu triplet	Δ	14.55	0.02	0.00	0.24	0	0	0
tipict	Δ (%)	2.90	0.30	0.00	2.60	0	0	0
Cys-Cu	Opt	508.93	5.99	8.84	9.61	90	90	90
open-shell singlet	Δ	8.28	-0.03	0.00	0.21	0	0	0
	Δ (%)	1.70	-0.60	0.00	2.20	0	0	0
Cys-Zn closed shell	Opt	515.80	6.01	8.90	9.65	90	90	90
	Δ	15.16	-0.02	0.06	0.25	0	0	0
	Δ (%)	3.00	-0.30	0.70	2.70	0	0	0
Cys-Zn open-shell singlet	Opt	518.46	6.01	8.90	9.70	90	90	90
	Δ	17.81	-0.02	0.06	0.30	0	0	0
	Δ (%)	3.60	-0.30	0.70	3.20	0	0	0
Cys metal- free	Opt	485.21	5.32	8.68	10.51	90	90	90
	Δ	-15.43	-0.71	-0.16	1.11	0	0	0
	Δ (%)	-3.10	-11.70	-1.80	11.80	0	0	0

S3. Exploration of the relative energetic stability of different spin states

The PBE-calculated relative stabilities of the different spin states of each metal-amino-acid crystal follow the same trend as the HSE results, which are discussed in sections 3.2 and 3.3 of the main text. As HSE is considered to be more accurate than PBE with respect to electronic structure and total energy estimations,² we only discuss qualitative trends involving the PBE results.

As can be seen in Tables S3 and S4, for Phe-Cu, the open-shell singlet state is more stable than the triplet state, and for Phe-Zn, the closed shell state is more stable than the open-shell singlet state. For the Cys-Cu crystal, the triplet state is more stable than the open-shell singlet state, and for Cys-Zn, the open-shell singlet converged to the closed shell state. This trend is also observed in the HSE calculations.

	Spin state	Total energy PBE (eV/unit cell)	Total energy HSE (eV/unit cell)	
Dha Cu	Triplet	-574.3094	-671.8333	
File-Cu	Open-shell singlet	-574.4667	-671.8381	
Dha 7a	Closed shell	-578.8950	-675.9831	
File-Zii	Open-shell singlet	-578.8868	-675.4627	
Phe metal-free	Closed shell	-565.3456	-666.3846	
Phe monoclinic	Closed shell	-583.6877	-687.6165	

Table S3. Total energies of optimized phenylalanine-based structures, calculated at various spin states using the PBE and HSE density functional approximations.

Table S4. Total energies of optimized cysteine-based structures, calculated at various spin states using the PBE and HSE density functional approximations.

	Spin state	Total energy PBE (eV/unit cell)	Total energy HSE (eV/unit cell)	
	Triplet	-305.9886	-363.7231	
Cys-Cu	Open-shell singlet	-305.8925	-363.5736	
Cue Zn	Closed shell	-306.5428	-364.6206	
Cys-Zii	Open-shell singlet	-306.5428	-364.6206	
Cys metal-free	Closed shell	-288.5296	-345.1836	
Cys monoclinic	Closed shell	-322.6445	-386.9864	

In the main text we describe the Gibbs free energy of formation as a method to compare relative stabilities of the crystals under study. Table S5 details the elemental chemical potentials used in the calculations.

Table S5. Chemical potential (μ) of each element used for free energy of formation (ΔG) calculations, as calculated using the HSE functional.

Element	Bulk structure	μ (eV/atom)
	Diamond cubic crystal	
С	($Fd\overline{3}m$ space group)	-9.10
Н	H ₂ molecule	-3.39
Ν	N ₂ molecule	-8.33
0	0 ₂ molecule (triplet state)	-4.37
	Orthorhombic crystal	
S	(<i>Fdddz</i> space group)	-4.12
	Face centered cubic crystal	
Cu	(<i>cF</i> 4 space group)	-0.67
	Hexagonal close packed	
Zn	crystal (<i>hP</i> 2 space group)	-1.53

S4. Supplemental refractive index calculations

In the main text, we presented refractive index values for the most stable spin configuration of each crystal, calculated using the HSE functional. For completeness, Table S6 provides the refractive index results obtained for each relevant spin state of the various crystals studied, calculated using both PBE and HSE.

Table S6. Refractive index values calculated for the bio-inspired crystals considered in the present study at different spin states, using the PBE and HSE exchange-correlation density functional approximations.

		PBE			HSE				
	Spin state	х	У	z	average	x	у	z	average
Dhe Cu	Triplet	1.68	1.75	1.82	1.75	1.61	1.61	1.70	1.64
	Open-shell singlet	1.64	1.64	1.75	1.68	1.60	1.60	1.69	1.63
Phe-7n	Closed shell	1.65	1.66	1.75	1.69	1.62	1.62	1.71	1.65
FIIC-ZII	Open-shell singlet	1.66	1.66	1.75	1.69	1.62	1.62	1.71	1.65
Phe metal-free	Closed shell	1.61	1.56	1.70	1.62	1.65	1.59	1.73	1.66
Phe monoclinic	Closed shell	1.63	1.52	1.70	1.62	1.65	1.55	1.74	1.65
Cys-Cu	Triplet	1.79	1.72	1.75	1.75	1.77	1.69	1.72	1.73
	Open-shell singlet		Μ	1etallic			Μ	letallic	
Cys-Zn	Closed shell	1.79	1.75	1.80	1.78	1.73	1.69	1.74	1.72
	Open-shell singlet	1.79	1.75	1.80	1.78	1.73	1.69	1.74	1.72
Cys metal-free	Closed shell	1.63	1.65	1.73	1.67	1.66	1.60	1.70	1.65
Cys monoclinic	Closed shell	1.58	1.64	1.63	1.62	1.55	1.61	1.59	1.58

The PBE functional is generally considered to be less accurate than HSE in terms of electronic structure (which is needed to calculate the dielectric response of the system) for metal-organic complexes. Therefore, we only comment on these results qualitatively. The average RI values calculated for the various crystals using PBE mostly follow the same trend as those obtained with HSE, except for Phe-Cu. For this crystal, the PBE-calculated RI of the triplet state is higher than that of the open-shell singlet, while for HSE, the two spin states possess similar RI values. We attribute this discrepancy to the better description of the electronic structure provided by HSE. As is evident from the Phe monoclinic RI of 1.62, which shows good agreement with experimental results³, the incorporation of metallic ions into the structure significantly increases the RI.

S5. References

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- (3) McMeekin, T. L.; Groves, M. L.; Hipp, N. J. Refractive Indices of Amino Acids, Proteins, and Related Substances. In *Advances in Chemistry*; 1964; pp 54–66.