Supporting Information

Influence of acid-base equilibrium on interactions of some monofunctional coumarin Pd(II) complexes with biologically relevant nucleophiles-comprehensive kinetic study

Žiko Milanović[a,*], Zoran Marković[a,b], Ana Kesić[a], Snežana Jovanović Stević[c], Biljana Petrović[d], Edina Avdović[a]

[a]*University of Kragujevac, Institute of Information Technologies, Department of Science, Jovana Cvijića bb, 34000 Kragujevac, Serbia*

[b]*Department of Natural Science and Mathematics, State University of Novi Pazar, Vuka Karadžića bb, 36300, Novi Pazar, Serbia*

[c]*University of Kragujevac, Faculty of Medical Sciences, Department of Pharmacy, Svetozara Markovića 69, 34000 Kragujevac, Serbia*

[d]*University of Kragujevac, Faculty of Science, Department of Chemistry, Radoja Domanovića 12, 34000 Kragujevac, Serbia*

***Corresponding author's e-mail address:** ziko.milanovic@uni.kg.ac.rs

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To quantify the molar fractions of acid-base species, the relationship between the acid constants (*Ka*) and the pK_a values as well as the expression for the equilibrium constant of the deprotonation process was used:

$$Ka_1 = 10^{-pKa1} \tag{1s}$$

$$Ka_2 = 10^{-pKa2} \tag{2s}$$

$$Ka_3 = 10^{-pKa3} \tag{3s}$$

$$Ka_4 = 10^{-pKa4} \tag{4s}$$

$$Ka_1 = \frac{\left[A_n - R^-\right]\left[H^+\right]}{\left[A_n - RH\right]} \tag{5s}$$

$$Ka_2 = \frac{\left[A_n - R^{2-}\right]\left[H^+\right]}{\left[A_n - R^-\right]} \tag{6s}$$

$$Ka_3 = \frac{\left[A_n - R^{3-}\right]\left[H^+\right]}{\left[A_n - R^{2-}\right]} \tag{7s}$$

$$Ka_4 = \frac{\left[A_n - R^{4-}\right]\left[H^+\right]}{\left[A_n - R^{3-}\right]} \tag{8s}$$

Molar fractions (*f*) of the represented acid-base species, were calculated using the following equations:

$$f(A_n - R^{4-}) = \frac{1}{1 + \beta_1\left[H^+\right] + \beta_2\left[H^+\right]^2 + \beta_2\left[H^+\right]^2 + \beta_4\left[H^+\right]^4} \quad (9s)$$

$$f(A_n - R^{3-}) = \beta_1\left[H^+\right] f(A_n - R^{4-}) \quad (10s)$$

$$f(A_n - R^{2-}) = \beta_2\left[H^+\right]^2 f(A_n - R^{3-}) \quad (11s)$$

$$f(A_n - R^{-}) = \beta_3\left[H^+\right]^3 f(A_n - R^{2-}) \quad (12s)$$

where $[H^+]$ represents the concentration of hydrogen ions at physiological pH in this case ($[H^+]=3.98\times10^{-8}$ M), while β represents global formation equilibrium constants:

$$\beta_1 = 10^{pKa4} \quad (13s)$$

$$\beta_2 = 10^{pKa4+pKa3} \quad (14s)$$

$$\beta_3 = 10^{pKa4+pKa3+pKa2} \quad (15s)$$

$$\beta_4 = 10^{pKa4+pKa3+pKa2+pKa1} \quad (16s)$$

Table S1. Observed *pseudo-first-order* rate constants as a function of ligand concentration for the substitution reactions between complex **C1** and **L-Cys** in 25 mM Hepes buffer and 50 mM NaCl (pH = 7.2) at 288 K and 298 K.

Ligand	**T [K]**	**λ [nm]**	**10^3 C_L [M]**	**k_{obsd} [s^{-1}]**
L-Cys	288	260	1	53.85(6)[a]
			2	97.80(6)
			3	140.66(5)
			4	200.34(4)
			5	246.45(5)
	298		1	61.10(4)
			2	112.68(6)
			3	171.90(5)
			4	230.10(6)
			5	290.70(5)

[a]Number of runs in parenthesis

Table S2. Observed *pseudo-first-order* rate constants as a function of ligand concentration for the substitution reactions between complex **C1** and nucleophiles in 25 mM Hepes buffer and 50 mM NaCl (pH = 7.2) at 310 K.

Nucleophile	**λ/nm**	**10^3C_L/M**	**k_{obsd}/s^{-1}**
L-Cys	260	1	68.98(6)[a]
		2	160.05(5)
		3	250.58(5)
		4	307.36(6)
		5	374.06(5)
L-Met	285	1	14.83(4)
		2	31.52(5)
		3	45.90(5)
		4	61.47(4)
		5	76.33(6)
5'-GMP	315	1	2.90(4)
		2	5.20(6)
		3	7.29(4)
		4	10.57(6)
		5	13.10(5)

[a]Number of runs in parenthesis.

Table S3. Observed *pseudo-first-order* rate constants as a function of ligand concentration for the substitution reactions between complex **C2** and **L-Cys** in 25 mM Hepes buffer and 50 mM NaCl (pH = 7.2) at 288 K and 298 K.

Ligand	**T [K]**	**λ [nm]**	**10^3 C_L [M]**	**k_{obsd} [s^{-1}]**
L-Cys	288	265	1	76.60(5)[a]
			2	138.44(6)
			3	208.10(5)
			4	278.54(5)
			5	347.90(5)
	298		1	87.20(5)
			2	160.77(6)
			3	255.50(5)
			4	320.68(4)
			5	408.80(5)

[a]Number of runs in parenthesis

Table S4. Observed *pseudo-first-order* rate constants as a function of ligand concentration for the substitution reactions between complex **C2** and nucleophiles in 25 mM Hepes buffer and 50 mM NaCl (pH = 7.2) at 310 K.

Nucleophile	λ/nm	10^3C_L/M	k_{obsd}/s^{-1}
		1	97.74(5)[a]
		2	232.70(5)
L-Cys	265	3	393.94(5)
		4	460.87(4)
		5	551.49(5)
		1	23.91(5)
		2	43.60(5)
L-Met	280	3	64.05(5)
		4	85.89(4)
		5	112.56(6)
		1	6.39(5)
		2	13.66(6)
5'-GMP	320	3	20.59(6)
		4	25.70(6)
		5	32.88(5)

[a]Number of runs in parenthesis.

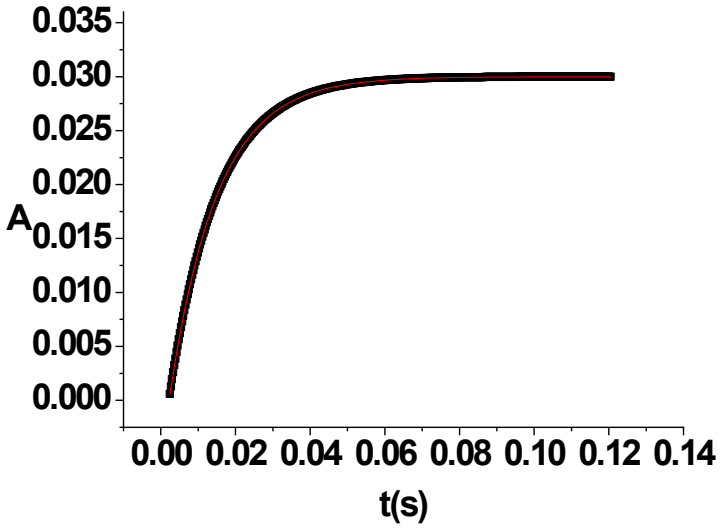

Figure S1. Kinetic trace for the reaction of **C2** complex ($1x10^{-4}$M) with **L-Met** ($4x10^{-3}$M) at pH = 7.2 (25 mM Hepes with addition 50 mM NaCl) and 310 K.

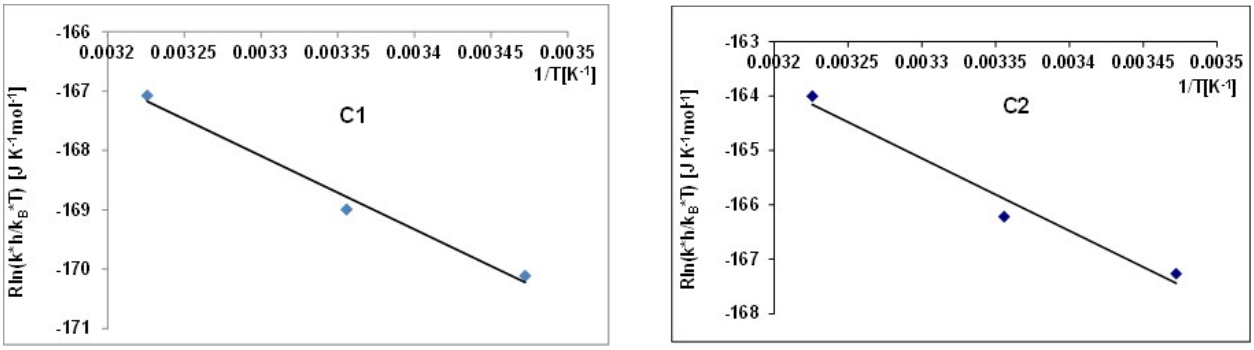

Figure S2. Eyring plots for the reaction of **C1** and **C2** with **L-Cys** at pH = 7.2 (25 mM HEPES with addition 50mM NaCl).

Table S5. Molar fractions (*f, %*) of differently represented acid-base species of **L–Cys** amino acid at different pH values.

pH	**L-Cys^{+}**	**L-Cys**	**L-Cys^{-}**	**L-Cys^{2-}**
0.0	99.12	0.88	0.00	0.00
1.0	91.82	8.18	0.00	0.00
2.0	52.88	47.12	0.00	0.00
3.0	10.09	89.91	0.00	0.00
4.0	1.11	98.88	0.01	0.00
5.0	0.11	99.79	0.10	0.00
6.0	0.01	99.00	0.99	0.00
7.0	0.00	90.90	9.09	0.01
7.2	**0.00**	**86.31**	**13.68**	**0.01**
8.0	0.00	49.86	49.86	0.28
9.0	0.00	8.65	86.49	4.86
10.0	0.00	0.64	63.60	35.76
11.0	0.00	0.02	15.10	84.89
12.0	0.00	0.00	1.75	98.25
13.0	0.00	0.00	0.18	99.82
14.0	0.00	0.00	0.02	99.98

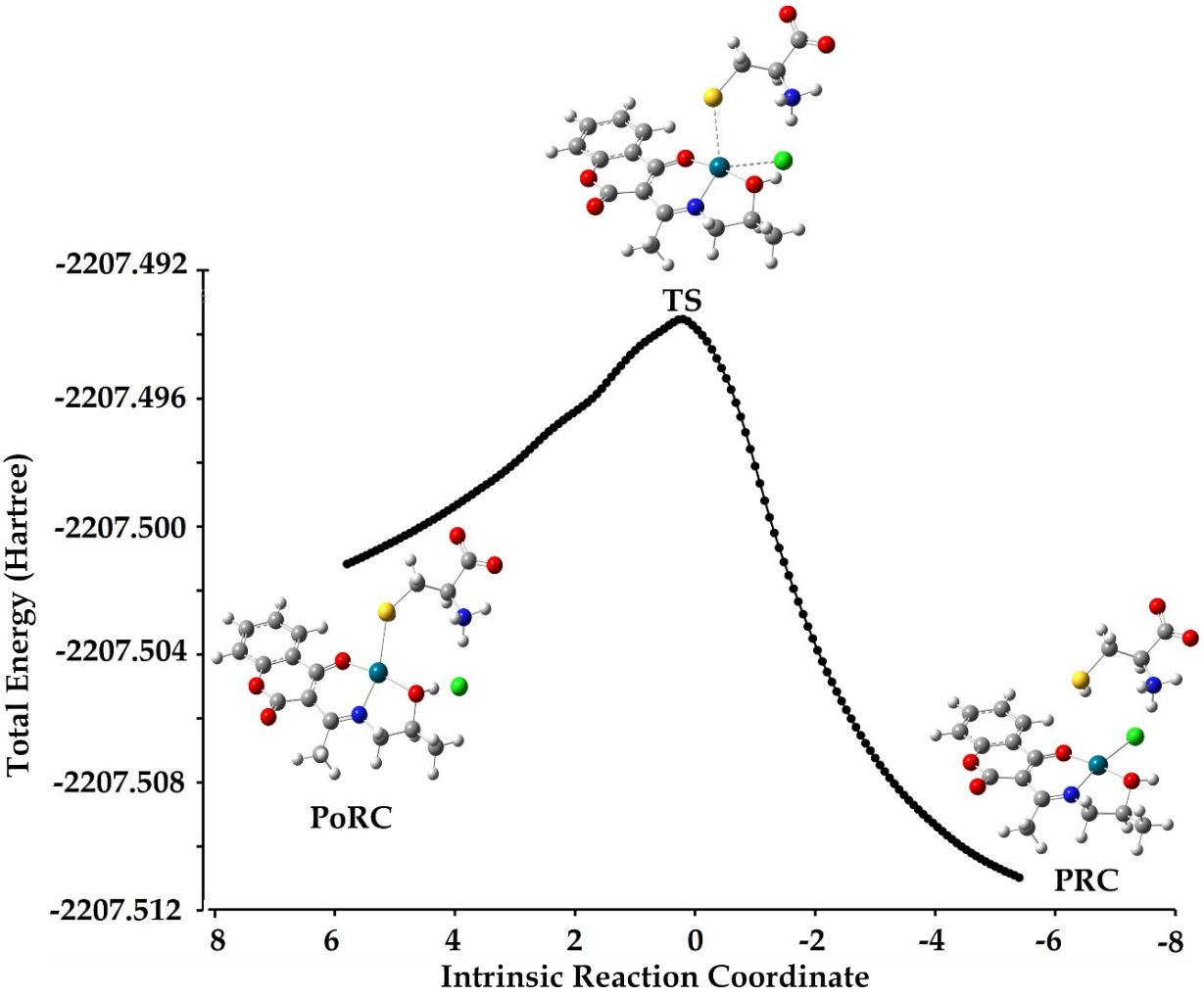

Figure S3. Intrinsic Reaction Coordinate (IRC) diagrams connecting the **C1-SH–Cys** transition state (TS) with two minima: *pre*-reaction (PRC) and *post*-reaction (PoRC) complexes on the singlet potential energy surface obtained with M06-2X functional in conjunction with 6–311++G(d,p) basis set C, N, O, Cl, and H/def2-TZVPD, triple-zeta-valence, basis set for atom Pd. Legend: grey – carbon atom, white – hydrogen atom, red – oxygen atom, blue – nitrogen atom, yellow – sulfur.

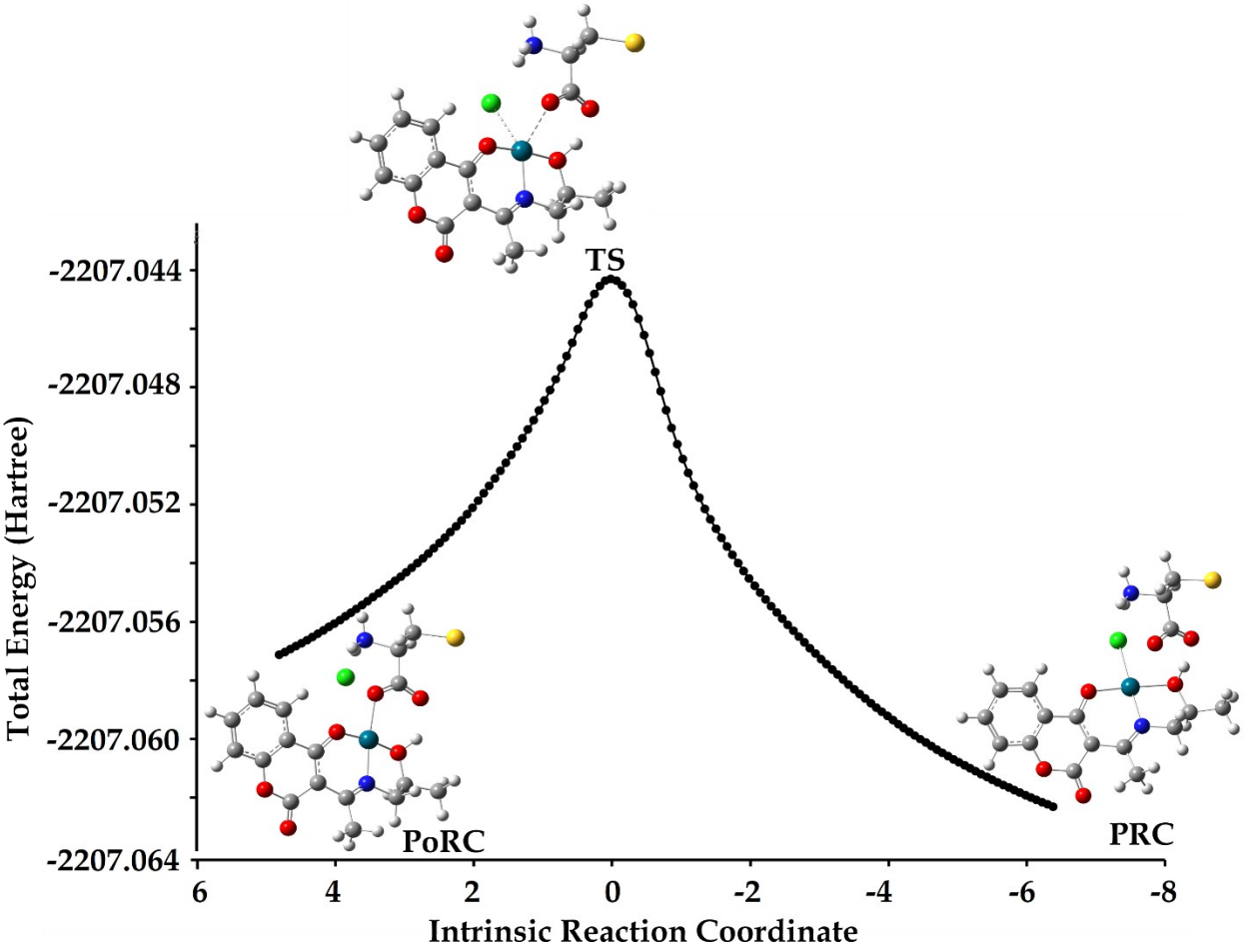

Figure S4. Intrinsic Reaction Coordinate (IRC) diagrams connecting the **C1-O–Cys**$^{-}$ transition state (TS) with two minima: *pre*-reaction (PRC) and *post*-reaction (PoRC) complexes on the singlet potential energy surface obtained with M06-2X functional in conjunction with 6–311++G(d,p) basis set C, N, O, Cl, and H/def2-TZVPD, triple-zeta-valence, basis set for atom Pd. Legend: grey – carbon atom, white – hydrogen atom, red – oxygen atom, blue – nitrogen atom, yellow – sulfur.

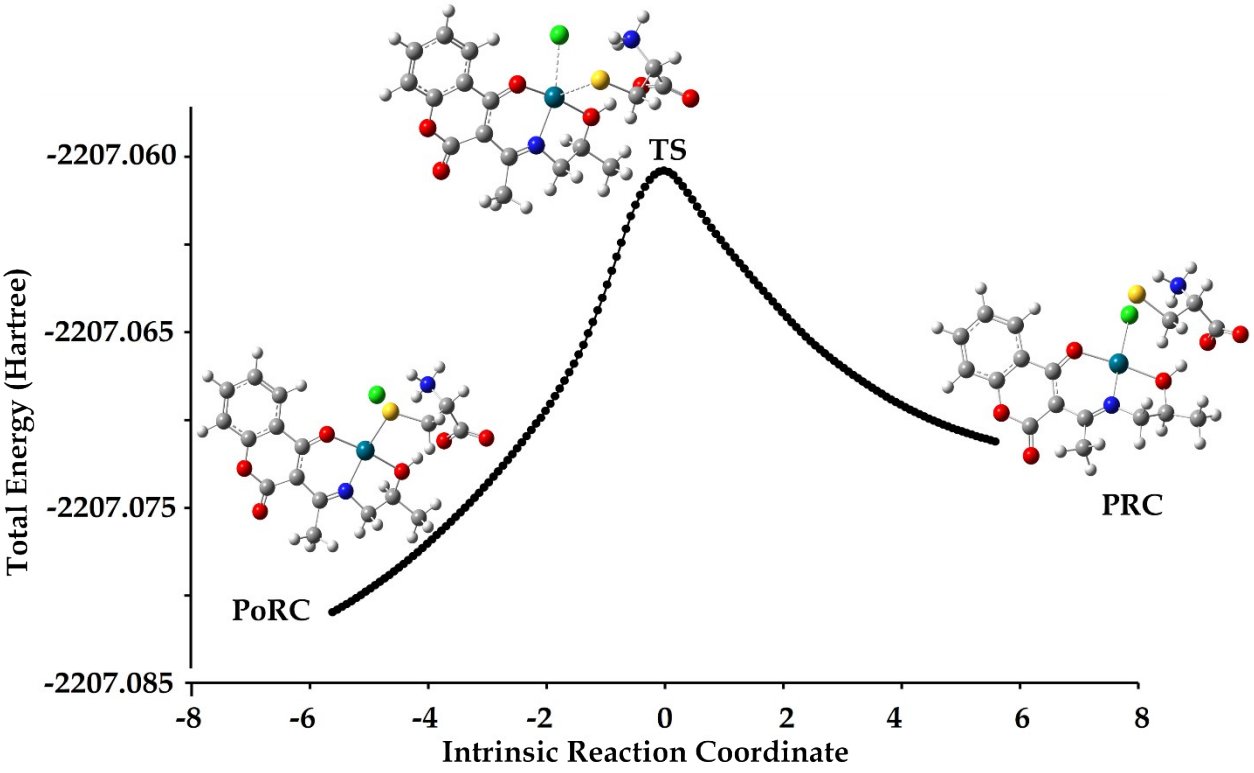

Figure S5. Intrinsic Reaction Coordinate (IRC) diagrams connecting the **C1-S–Cys**$^{-}$ transition state (TS) with two minima: *pre*-reaction (PRC) and *post*-reaction (PoRC) complexes on the singlet potential energy surface obtained with M06-2X functional in conjunction with 6–311++G(d,p) basis set C, N, O, Cl, and H/def2-TZVPD, triple-zeta-valence, basis set for atom Pd. Legend: grey – carbon atom, white – hydrogen atom, red – oxygen atom, blue – nitrogen atom, yellow – sulfur.

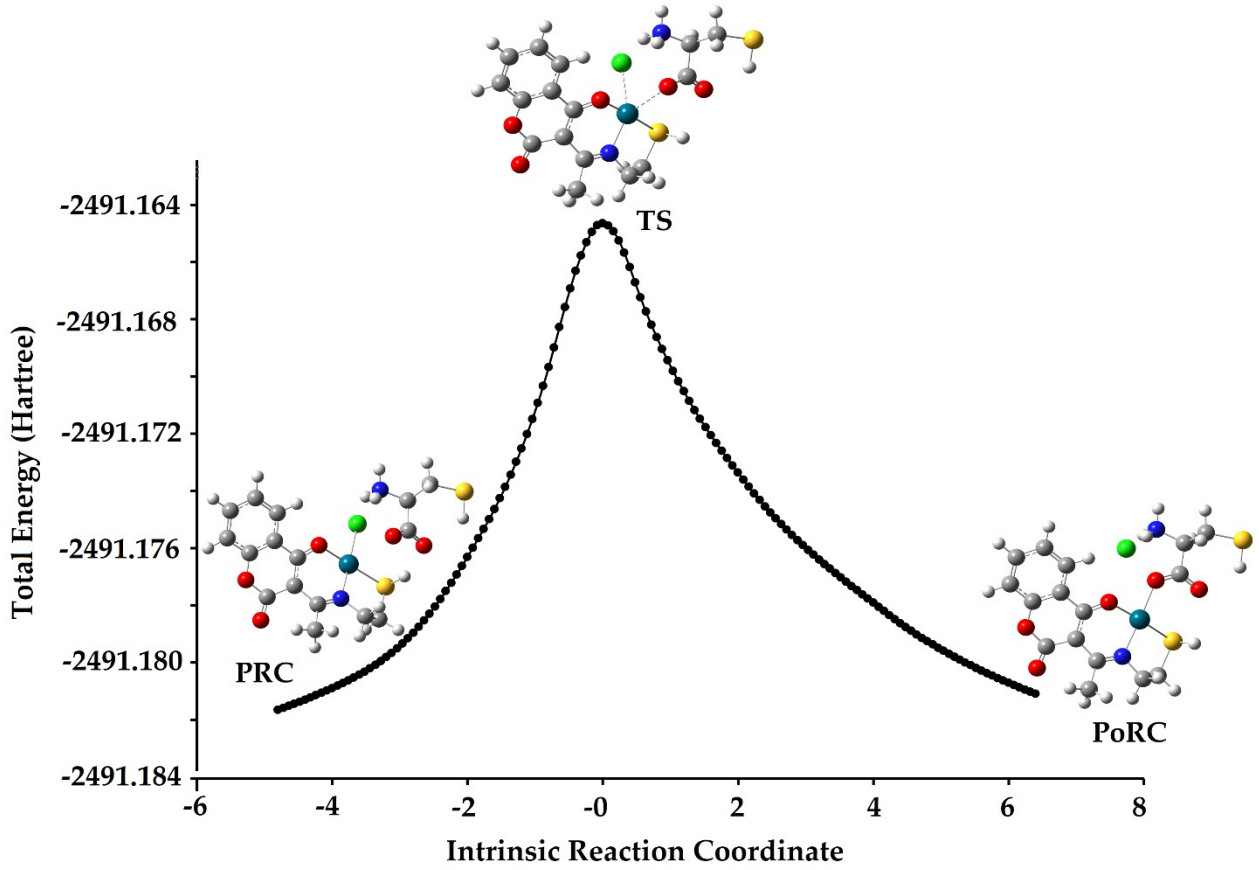

Figure S6. Intrinsic Reaction Coordinate (IRC) diagrams connecting the **C2-O–Cys** transition state (TS) with two minima: *pre*-reaction (PRC) and *post*-reaction (PoRC) complexes on the singlet potential energy surface obtained with M06-2X functional in conjunction with 6–311++G(d,p) basis set C, N, O, Cl, and H/def2-TZVPD, triple-zeta-valence, basis set for atom Pd. Legend: grey – carbon atom, white – hydrogen atom, red – oxygen atom, blue – nitrogen atom, yellow – sulfur.

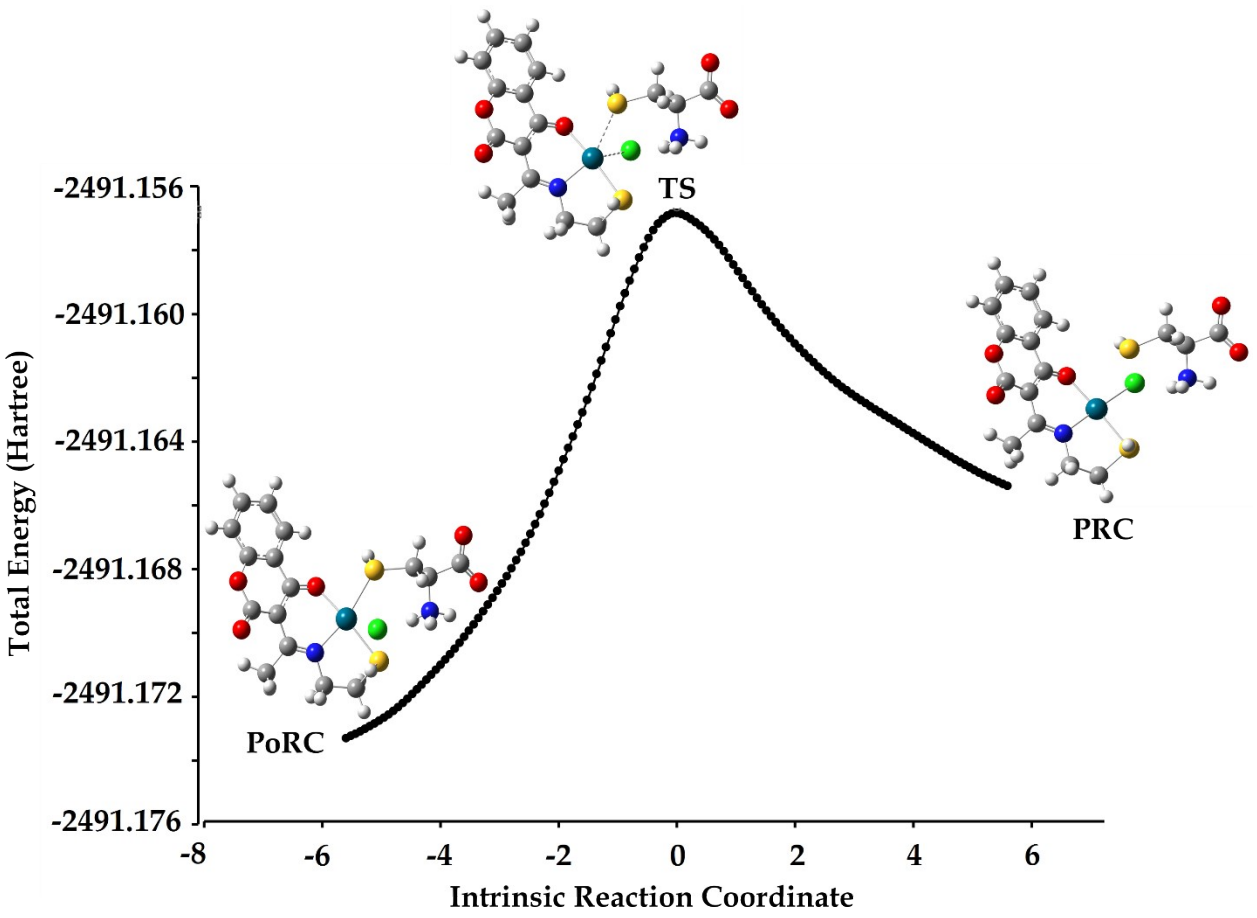

Figure S7. Intrinsic Reaction Coordinate (IRC) diagrams connecting the **C2-SH–Cys** transition state (TS) with two minima: *pre*-reaction (PRC) and *post*-reaction (PoRC) complexes on the singlet potential energy surface obtained with M06-2X functional in conjunction with 6–311++G(d,p) basis set C, N, O, Cl, and H/def2-TZVPD, triple-zeta-valence, basis set for atom Pd. Legend: grey – carbon atom, white – hydrogen atom, red – oxygen atom, blue – nitrogen atom, yellow – sulfur.

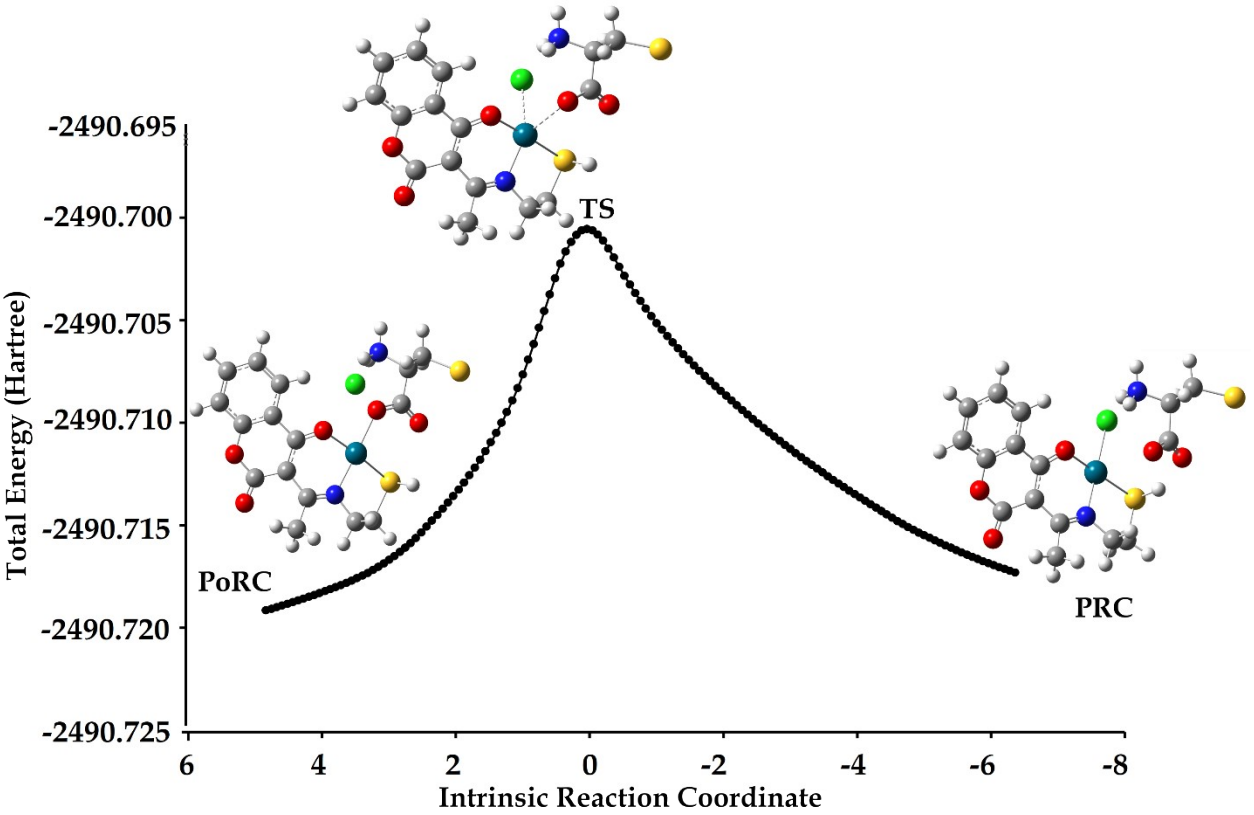

Figure S8. Intrinsic Reaction Coordinate (IRC) diagrams connecting the **C2-O–Cys**$^{-}$ transition state (TS) with two minima: *pre*-reaction (PRC) and *post*-reaction (PoRC) complexes on the singlet potential energy surface obtained with M06-2X functional in conjunction with 6–311++G(d,p) basis set C, N, O, Cl, and H/def2-TZVPD, triple-zeta-valence, basis set for atom Pd. Legend: grey – carbon atom, white – hydrogen atom, red – oxygen atom, blue – nitrogen atom, yellow – sulfur.

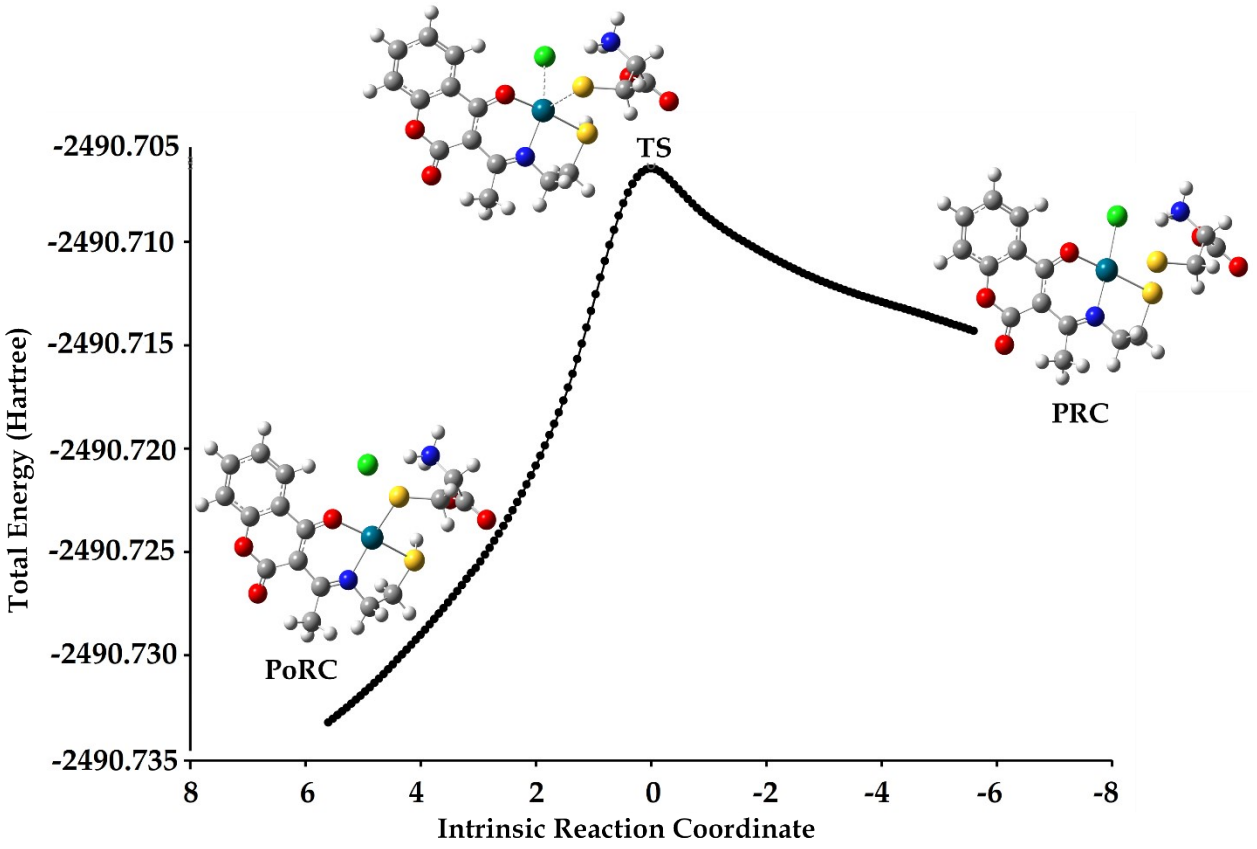

Figure S9. Intrinsic Reaction Coordinate (IRC) diagrams connecting the **C2-S–Cys**$^{-}$ transition state (TS) with two minima: *pre*-reaction (PRC) and *post*-reaction (PoRC) complexes on the singlet potential energy surface obtained with M06-2X functional in conjunction with 6–311++G(d,p) basis set C, N, O, Cl, and H/def2-TZVPD, triple-zeta-valence, basis set for atom Pd. Legend: grey – carbon atom, white – hydrogen atom, red – oxygen atom, blue – nitrogen atom, yellow – sulfur.

Table S6. Summed total energies (*G* (Hartree)) of reaction participants (local minima and maxima) obtained from IRC calculations

Acid-base species	**C1** (Total energy, *G* (Hartree))		
	PRC	TS	PoRC
O–Cys	-2207.523801	-2207.506403	-2207.519360
HS–Cys	-2207.510977	-2207.493530	-2207.501181
O–Cys$^-$	-2207.062323	-2207.044306	-2207.058538
S–Cys$^-$	-2207.071232	-2207.055804	-2207.080959
Acid-base species	**C2** (Total energy, *G* (Hartree))		
	PRC	TS	PoRC
O–Cys	-2491.181094	-2491.164646	-2491.182575
HS–Cys	-2491.173520	-2491.157053	-2491.165609
O–Cys$^-$	-2490.717309	-2490.700565	-2490.720320
S–Cys$^-$	-2490.714322	-2490.706464	-2490.733251

Table S7. The bond length of the interest, the Wiberg bond indices (WBIs), natural atomic charges (NACs), total natural populations (TNPs, in parentheses), and natural electron (NECs) of selected atoms/ions for transition states (TS) of **C1** compound

O–Cys					**HS–Cys**				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**

Pd-O_3	0.4613	Pd	0.826	45.174	Pd-O_3	0.4578	Pd	0.803	45.192
Pd-$O_{4"}$	0.3345	O_3	-0.641	8.641	Pd-$O_{4"}$	0.2887	O_3	-0.647	8.647
Pd-$N_{1"}$	0.5552	$O_{4"}$	-0.745	8.745	Pd-$N_{1"}$	0.5581	$O_{4"}$	-0.723	8.723
Pd-Cl_1	0.2160	$N_{1"}$	-0.479	7.470	Pd-Cl_1	0.1922	$N_{1"}$	-0.476	7.476
		Cl_1	-0.805	17.805			Cl_1	-0.812	17.812
Pd-O_{Cys}	0.1794	O_{Cys}	-0.768	8.768	Pd-S_{Cys}	0.2481	S_{Cys}	0.029	15.971
NEC	Pd[core]$5s^{0.25}4d^{8.63}$ $5p^{0.29}$ $5d^{0.01}$				Pd[core]$5s^{0.25}4d^{8.67}$ $5p^{0.27}$ $5d^{0.01}$				
	O_3[core]$2s^{1.64}2p^{4.97}$ $3p^{0.01}$				O_3[core]$2s^{1.65}2p^{4.98}$ $3p^{0.01}4p^{0.01}$				
	$O_{4"}$[core]$2s^{1.63}2p^{5.10}$ $4p^{0.01}$				$O_{4"}$[core]$2s^{1.66}2p^{5.05}$ $3p^{0.01}4p^{0.01}$				
	$N_{1"}$[core]$2s^{1.29}2p^{4.15}$ $3p^{0.01}$ $4p^{0.01}$				$N_{1"}$[core]$2s^{1.29}2p^{4.16}3p^{0.01}$ $4p^{0.01}$				
	Cl_1[core]$3s^{1.96}3p^{5.85}$				Cl_1[core]$3s^{1.96}3p^{5.85}$				
	O_{Cys}[core]$2s^{1.69}2p^{5.06}$ $3p^{0.01}$				S_{Cys}[core]$3s^{1.68}3p^{4.26}$ $3d^{0.02}$				
O–Cys$^-$					**S–Cys$^-$**				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.4539	Pd	0.821	45.179	Pd-O_3	0.4630	Pd	0.712	45.288
Pd-$O_{4"}$	0.3539	O_3	-0.642	8.643	Pd-$O_{4"}$	0.3522	O_3	-0.632	8.632
Pd-$N_{1"}$	0.5481	$O_{4"}$	-0.749	8.749	Pd-$N_{1"}$	0.4931	$O_{4"}$	-0.772	7.489
Pd-Cl_1	0.2173	$N_{1"}$	0.472	7.472	Pd-Cl_1	0.3341	$N_{1"}$	-0.489	8.773
		Cl_1	-0.817	17.817			Cl_1	-0.782	17.782
Pd-O_{Cys}	0.1892	O_{Cys}	-0.749	8.775	Pd-S_{Cys}	0.2997	S_{Cys}	-0.539	16.539
NEC	Pd[core]$5s^{0.25}4d^{8.63}$ $5p^{0.29}$ $5d^{0.01}$				Pd[core]$5s^{0.26}4d^{8.64}$ $5p^{0.37}$ $5d^{0.01}$				
	O_3[core]$2s^{1.64}2p^{4.98}$ $3p^{0.01}$				O_3[core]$2s^{1.64}2p^{4.97}$ $3p^{0.01}4p^{0.01}$				
	$O_{4"}$[core]$2s^{1.63}2p^{5.10}$ $3p^{0.01}$				$O_{4"}$[core]$2s^{1.62}2p^{5.13}$ $3p^{0.01}4p^{0.01}$				
	$N_{1"}$[core]$2s^{1.29}2p^{4.16}$ $4p^{0.01}$				$N_{1"}$[core]$2s^{1.30}2p^{4.17}3p^{0.01}$ $4p^{0.01}$				
	Cl_1[core]$3s^{1.96}3p^{5.85}$				Cl_1[core]$3s^{1.94}3p^{5.84}$				
	O_{Cys}[core]$2s^{1.69}2p^{5.06}$ $3p^{0.01}$				S_{Cys}[core]$3s^{1.78}3p^{4.73}$ $3d^{0.01}$				

Table S8. The bond length of the interest, the Wiberg bond indices (WBIs), natural atomic charges (NACs), total natural populations (TNPs, in parentheses), and natural electron (NECs) of selected atoms/ions for transition states (TS) of **C2** compound

O–Cys					**HS–Cys**				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.4225	Pd	0.587	45.413	Pd-O_3	0.4262	Pd	0.514	45.486

Pd-$S_{4"}$	0.6194	O_3	-0.642	8.642	Pd-$S_{4"}$	0.6053	O_3	-0.648	8.648
Pd-$N_{1"}$	0.5156	$S_{4"}$	0.267	15.733	Pd-$N_{1"}$	0.5142	$S_{4"}$	0.257	15.743
Pd-Cl_1	0.2808	$N_{1"}$	-0.476	7.476	Pd-Cl_1	0.2640	$N_{1"}$	-0.480	7.480
		Cl_1	-0.768	17.768			Cl_1	-0.772	17.772
Pd-O_{Cys}	0.1776	O_{Cys}	-0.794	8.794	Pd-S_{Cys}	0.2976	S_{Cys}	0.055	15.945
NEC	Pd[core]$5s^{0.27}4d^{8.76}$ $5p^{0.37}$ $5d^{0.01}$				Pd[core]$5s^{0.29}4d^{8.79}$ $5p^{0.40}$ $5d^{0.01}$				
	O_3[core]$2s^{1.64}2p^{4.98}$ $3p^{0.01}$				O_3[core]$2s^{1.64}2p^{4.98}$ $3p^{0.01}4p^{0.01}$				
	$S_{4"}$[core]$3s^{1.65}3p^{4.05}3d^{0.02}$				$S_{4"}$[core] $3s^{1.65}3p^{4.06}3d^{0.02}$				
	$N_{1"}$[core]$2s^{1.30}2p^{4.15}$ $3p^{0.01}$ $4p^{0.01}$				$N_{1"}$[core]$2s^{1.30}2p^{4.15}3p^{0.01}$ $4p^{0.01}$				
	Cl_1[core]$3s^{1.95}3p^{5.82}$				Cl_1[core]$3s^{1.94}3p^{5.83}$				
	O_{Cys}[core]$2s^{1.70}2p^{5.08}$ $3p^{0.01}$				S_{Cys}[core]$3s^{1.67}3p^{4.24}$ $3d^{0.02}$				
O–Cys$^-$					**S–Cys$^-$**				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.4216	Pd	0.575	45.425	Pd-O_3	0.4195	Pd	0.436	45.564
Pd-$S_{4"}$	0.6257	O_3	-0.641	8.641	Pd-$S_{4"}$	0.6415	O_3	-0.639	8.639
Pd-$N_{1"}$	0.5079	$S_{4"}$	0.280	15.720	Pd-$N_{1"}$	0.4623	$S_{4"}$	0.273	15.727
Pd-Cl_1	0.3013	$N_{1"}$	-0.479	7.479	Pd-Cl_1	0.3911	$N_{1"}$	-0.489	7.489
		Cl_1	-0.764	17.764			Cl_1	-0.743	17.743
Pd-O_{Cys}	0.1800	O_{Cys}	-0.813	8.813	Pd-S_{Cys}	0.3323	S_{Cys}	-0.526	16.526
NEC	Pd[core]$5s^{0.27}4d^{8.76}$ $5p^{0.38}$ $5d^{0.01}$				Pd[core]$5s^{0.29}4d^{8.79}$ $5p^{0.47}$ $5d^{0.01}$				
	O_3[core]$2s^{1.64}2p^{4.98}$ $3p^{0.01}$				O_3[core]$2s^{1.64}2p^{4.98}$ $3p^{0.01}$				
	$S_{4"}$[core] $3s^{1.65}3p^{4.03}3p^{0.01}3d^{0.01}$				$S_{4"}$[core] $3s^{1.64}3p^{4.05}3d^{0.02}$				
	$N_{1"}$[core]$2s^{1.30}2p^{4.15}$ $3p^{0.01}$				$N_{1"}$[core]$2s^{1.30}2p^{4.16}3p^{0.01}$ $4p^{0.01}$				
	Cl_1[core]$3s^{1.94}3p^{5.82}$				Cl_1[core]$3s^{1.93}3p^{5.81}$				
	O_{Cys}[core]$2s^{1.70}2p^{5.09}3p^{0.01}$				S_{Cys}[core]$3s^{1.77}3p^{4.72}3d^{0.01}$				

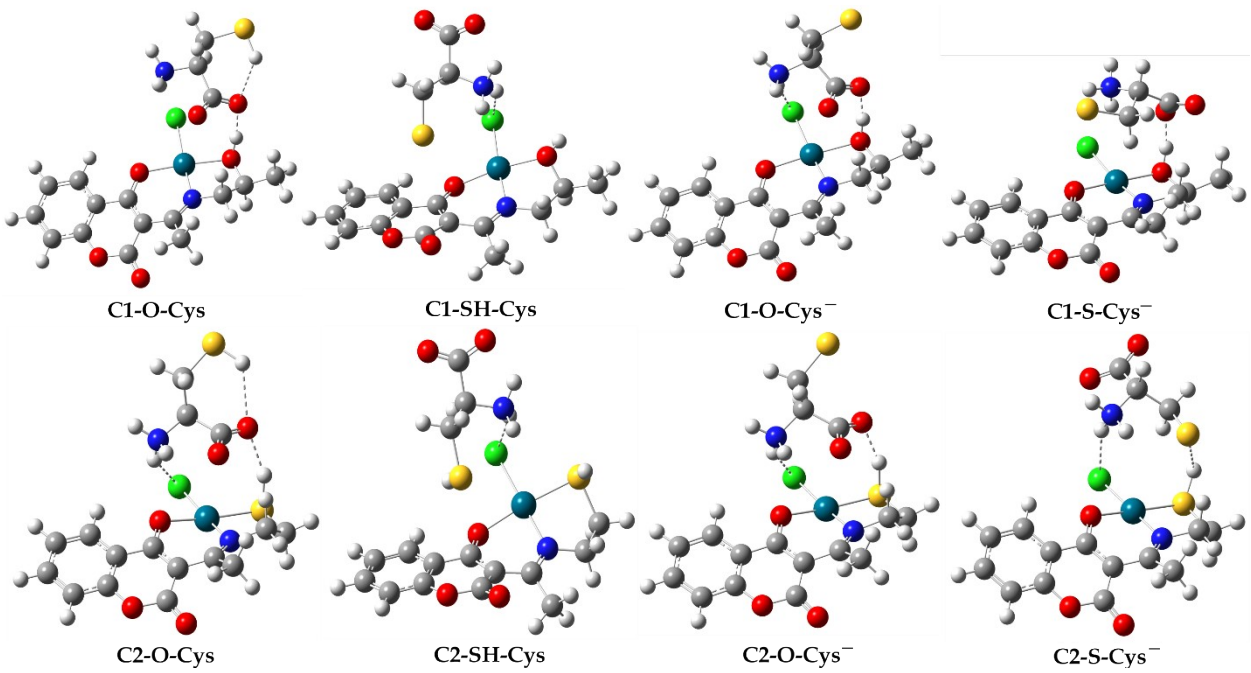

Figure S10. Optimized geometries of *pre*-reaction (**PRC**) complexes between the investigated compounds, **C1** and **C2**, and acid-base forms of **L-Cys**/**L-Cys**$^{-}$ with intramolecular hydrogen bond (interrupted line) obtained with M06-2X functional in conjunction with 6–311++G(d,p) basis set C, N, O, Cl, and H/def2-TZVPD, triple-zeta-valence, basis set for atom Pd theory in the water. Legend: grey – carbon atom, white – hydrogen atom, red – oxygen atom, blue – nitrogen atom, yellow – sulfur.

Table S9. The bond length of the interest, the Wiberg bond indices (WBIs), natural atomic charges (NACs), total natural populations (TNPs, in parentheses), and natural electron (NECs) of selected atoms/ions for *pre*-reaction complexes (PRC) of **C1** compound

O–Cys					**HS–Cys**				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.4349	Pd	0.742	45.258	Pd-O_3	0.4400	Pd	0.744	45.256
Pd-$O_{4"}$	0.3381	O_3	-0.648	8.648	Pd-$O_{4"}$	0.2928	O_3	-0.678	8.678
Pd-$N_{1"}$	0.5295	$O_{4"}$	-0.752	8.752	Pd-$N_{1"}$	0.5267	$O_{4"}$	-0.718	8.718
Pd-Cl_1	0.5000	$N_{1"}$	-0.477	7.477	Pd-Cl_1	0.5204	$N_{1"}$	-0.482	7.482
		Cl_1	-0.631	17.631			Cl_1	-0.628	17.628
Pd-O_{Cys}	0.0319	O_{Cys}	-0.755	8.755	Pd-S_{Cys}	0.0390	S_{Cys}	-0.054	16.054
NEC	Pd[core]$5s^{0.29}4d^{8.68}5p^{0.27}5d^{0.01}$				Pd[core]$5s^{0.29}4d^{8.86}5p^{0.27}5d^{0.01}$				
	O_3[core]$2s^{1.64}2p^{4.98}3p^{0.01}$				O_3[core]$2s^{1.65}2p^{4.99}3p^{0.01}4p^{0.01}$				
	$O_{4"}$[core]$2s^{1.64}2p^{5.09}3p^{0.01}$				$O_{4"}$[core]$2s^{1.65}2p^{5.05}3p^{0.01}$				
	$N_{1"}$[core]$2s^{1.29}2p^{4.16}3p^{0.01}$				$N_{1"}$[core]$2s^{1.29}2p^{4.16}3p^{0.01}4p^{0.01}$				
	Cl_1[core]$3s^{1.92}3p^{5.71}$				Cl_1[core]$3s^{1.92}3p^{5.71}$				
	O_{Cys}[core]$2s^{1.71}2p^{5.03}3p^{0.01}$				S_{Cys}[core]$3s^{1.70}3p^{4.32}3d^{0.01}$				
O–Cys$^-$					**S–Cys$^-$**				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.4294	Pd	0.738	45.261	Pd-O_3	0.4288	Pd	0.733	45.267
Pd-$O_{4"}$	0.3470	O_3	-0.650	8.650	Pd-$O_{4"}$	0.3357	O_3	-0.648	8.648
Pd-$N_{1"}$	0.5255	$O_{4"}$	-0.756	8.756	Pd-$N_{1"}$	0.5059	$O_{4"}$	-0.749	8.748
Pd-Cl_1	0.5068	$N_{1"}$	-0.476	7.476	Pd-Cl_1	0.5290	$N_{1"}$	-0.496	7.496
		Cl_1	-0.626	17.626			Cl_1	-0.627	17.627
Pd-O_{Cys}	0.0279	O_{Cys}	-0.770	8.770	Pd-S_{Cys}	0.0112	S_{Cys}	-0.721	16.721
NEC	Pd[core]$5s^{0.30}4d^{8.88}5p^{0.27}5d^{0.01}$				Pd[core]$5s^{0.30}4d^{8.68}5p^{0.27}5d^{0.01}$				
	O_3[core]$2s^{1.64}2p^{4.98}3p^{0.01}$				O_3[core]$2s^{1.64}2p^{4.98}3p^{0.01}$				
	$O_{4"}$[core]$2s^{1.64}2p^{5.10}3p^{0.01}$				$O_{4"}$[core]$2s^{1.64}2p^{5.09}3p^{0.01}$				
	$N_{1"}$[core]$2s^{1.29}2p^{4.16}3p^{0.01}$				$N_{1"}$[core]$2s^{1.29}2p^{4.17}3p^{0.01}4p^{0.01}$				
	Cl_1[core]$3s^{1.92}3p^{5.71}$				Cl_1[core]$3s^{1.91}3p^{5.71}$				
	O_{Cys}[core]$2s^{1.71}2p^{5.05}3p^{0.01}$				S_{Cys}[core]$3s^{1.82}3p^{4.87}3d^{0.01}$				

Table S10. The bond length of the interest, the Wiberg bond indices (WBIs), natural atomic charges (NACs), total natural populations (TNPs, in parentheses), and natural electron (NECs) of selected atoms/ions for *pre*-reaction complexes (PRC) of **C2** compound

O–Cys					HS–Cys				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.3731	Pd	0.486	45.514	Pd-O_3	0.3831	Pd	0.519	45.481
Pd-$S_{4"}$	0.6175	O_3	-0.690	8.690	Pd- $S_{4"}$	0.5947	O_3	-0.692	8.692
Pd-$N_{1"}$	0.4938	$S_{4"}$	0.216	15.784	Pd-$N_{1"}$	0.5002	$S_{4"}$	0.252	16.056
Pd-Cl_1	0.5563	$N_{1"}$	-0.471	7.471	Pd-Cl_1	0.5405	$N_{1"}$	-0.485	7.484
		Cl_1	-0.587	17.587			Cl_1	-0.594	17.594
Pd-O_{Cys}	0.0373	O_{Cys}	-0.780	8.780	Pd-S_{Cys}	0.0416	S_{Cys}	-0.056	16.056
NEC	Pd[core]$5s^{0.33}4d^{8.83}5p^{0.34}\,5d^{0.01}$				Pd[core]$5s^{0.33}4d^{8.81}\,5p^{0.33}\,5d^{0.01}$				
	O_3[core]$2s^{1.65}2p^{5.01}3p^{0.01}$				O_3[core]$2s^{1.65}2p^{5.00}3p^{0.01}4p^{0.01}$				
	$S_{4"}$[core]$3s^{1.71}3p^{4.31}3d^{0.01}$				$S_{4"}$[core]$3s^{1.65}3p^{4.06}3d^{0.02}$				
	$N_{1"}$[core]$2s^{1.30}2p^{4.15}3p^{0.01}$				$N_{1"}$[core]$2s^{1.30}2p^{4.16}3p^{0.01}\,4p^{0.01}$				
	Cl_1[core]$3s^{1.90}3p^{5.68}$				Cl_1[core]$3s^{1.91}3p^{5.68}$				
	O_{Cys}[core]$2s^{1.71}2p^{5.05}3p^{0.01}$				S_{Cys}[core]$3s^{1.70}3p^{4.32}3d^{0.01}$				
$O–Cys^-$					**$S–Cys^-$**				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.3671	Pd	0.484	45.516	Pd-O_3	0.3789	Pd	0.503	45.497
Pd-$S_{4"}$	0.6284	O_3	-0.689	8.689	Pd- $S_{4"}$	0.6007	O_3	-0.662	8.661
Pd-$N_{1"}$	0.4917	$S_{4"}$	0.193	15.807	Pd-$N_{1"}$	0.4864	$S_{4"}$	0.251	15.749
Pd-Cl_1	0.5489	$N_{1"}$	-0.469	7.469	Pd-Cl_1	0.5453	$N_{1"}$	-0.483	7.483
		Cl_1	-0.589	17.589			Cl_1	-0.592	17.592
Pd-O_{Cys}	0.0354	O_{Cys}	-0.793	8.793	Pd-S_{Cys}	0.0669	S_{Cys}	-0.707	16.7070
NEC	Pd[core]$5s^{0.33}4d^{8.83}5p^{0.34}\,5d^{0.01}$				Pd[core]$5s^{0.33}4d^{8.82}5p^{0.34}\,5d^{0.01}$				
	O_3[core]$2s^{1.65}2p^{5.02}3p^{0.01}$				O_3[core]$2s^{1.65}2p^{4.99}3p^{0.01}$				
	$S_{4"}$[core]$3s^{1.64}3p^{4.13}3d^{0.02}$				$S_{4"}$[core]$3s^{1.66}3p^{4.06}3d^{0.02}$				
	$N_{1"}$[core]$2s^{1.30}2p^{4.14}3p^{0.01}$				$N_{1"}$[core]$2s^{1.30}2p^{4.16}3p^{0.01}$				
	Cl_1[core]$3s^{1.90}3p^{5.68}$				Cl_1[core]$3s^{1.90}3p^{5.68}$				
	O_{Cys}[core]$2s^{1.71}2p^{5.07}3p^{0.01}$				S_{Cys}[core]$3s^{1.81}3p^{4.87}3d^{0.01}$				

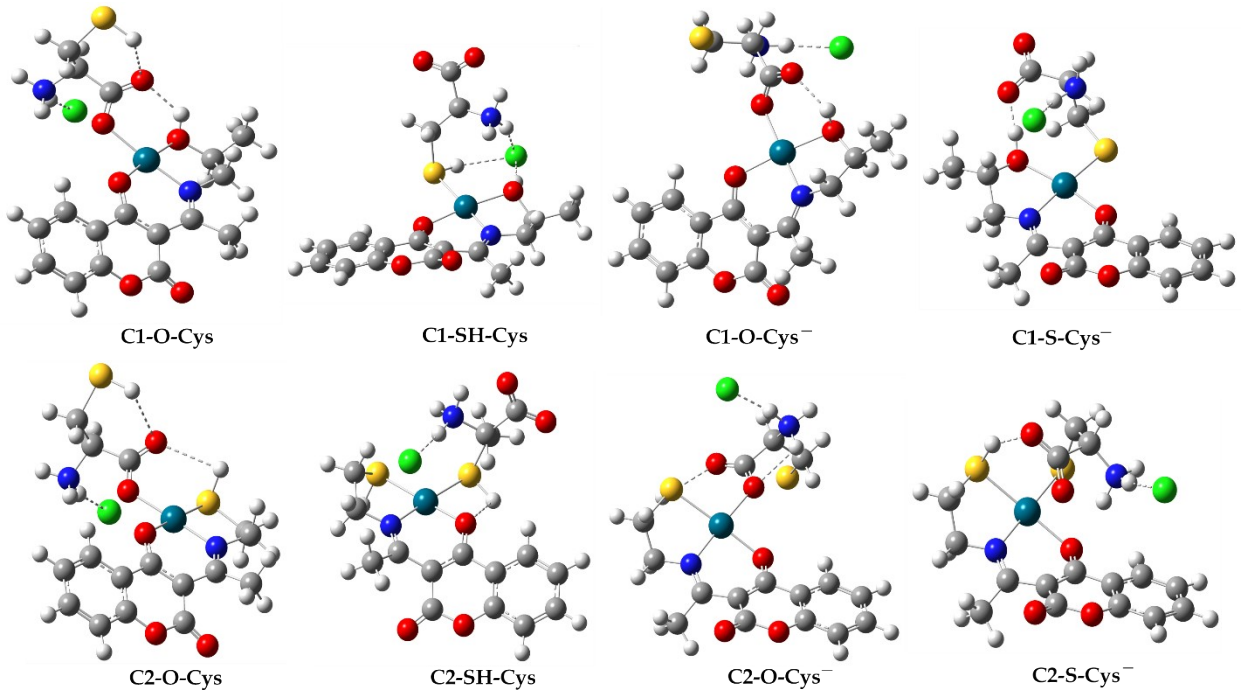

Figure S11. Optimized geometries of *post*-reaction (**PoRC**) complexes between the investigated compounds, **C1** and **C2**, and acid-base forms of **L-Cys**/**L-Cys**$^{-}$ with intramolecular hydrogen bond (interrupted line) obtained with M06-2X functional in conjunction with 6–311++G(d,p) basis set C, N, O, Cl, and H/def2-TZVPD, triple-zeta-valence, basis set for atom Pd theory in the water. Legend: grey – carbon atom, white – hydrogen atom, red – oxygen atom, blue – nitrogen atom, yellow – sulfur.

Table S11. The bond length of the interest, the Wiberg bond indices (WBIs), natural atomic charges (NACs), total natural populations (TNPs, in parentheses), and natural electron (NECs) of selected atoms/ions for *post*-reaction complexes (PoRC) of **C1** compound

O–Cys					HS–Cys				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.4347	Pd	0.885	45.115	Pd-O_3	0.4478	Pd	0.718	45.282
Pd-$O_{4"}$	0.3093	O_3	-0.652	8.652	Pd- $O_{4"}$	0.3220	O_3	-0.645	8.645
Pd-$N_{1"}$	0.5424	$O_{4"}$	-0.733	8.733	Pd-$N_{1"}$	0.5187	$O_{4"}$	-0.784	8.785
Pd-Cl_1	0.0023	$N_{1"}$	-0.483	7.483	Pd-Cl_1	0.0076	$N_{1"}$	-0.486	7.486
		Cl_1	-0.897	17.897			Cl_1	-0.836	17.834
Pd-O_{Cys}	0.3345	O_{Cys}	-0.756	8.756	Pd-S_{Cys}	0.5017	S_{Cys}	0.146	15.854
NEC	Pd[core]$5s^{0.28}4d^{8.62}5p^{0.20}5d^{0.01}$				Pd[core]$5s^{0.31}4d^{8.72}5p^{0.24}5d^{0.01}$				
	O_3[core]$2s^{1.65}2p^{4.98}3p^{0.01}$				O_3[core]$2s^{1.64}2p^{4.98}3p^{0.01}4p^{0.01}$				
	O_4[core]$2s^{1.64}2p^{5.08}3p^{0.01}$				O_4[core]$2s^{1.65}2p^{5.11}3p^{0.01}$				
	N[core]$2s^{1.29}2p^{4.17}3p^{0.01}$				N[core]$2s^{1.29}2p^{4.17}3p^{0.01}4p^{0.01}$				
	Cl[core]$3s^{1.98}3p^{5.91}$				Cl[core]$3s^{1.98}3p^{5.86}$				
	O[core]$2s^{1.68}2p^{5.05}3p^{0.01}$				S[core]$3s^{1.65}3p^{4.17}3d^{0.02}$				
O–Cys$^-$					**S–Cys$^-$**				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.4296	Pd	0.880	45.120	Pd-O_3	0.4016	Pd	0.616	45.384
Pd-$O_{4"}$	0.3126	O_3	-0.653	8.653	Pd- $O_{4"}$	0.3205	O_3	-0.662	8.662
Pd-$N_{1"}$	0.5357	$O_{4"}$	-0.735	8.735	Pd-$N_{1"}$	0.4167	$O_{4"}$	-0.777	8.777
Pd-Cl_1	0.0016	$N_{1"}$	-0.484	7.484	Pd-Cl_1	0.0442	$N_{1"}$	-0.503	7.503
		Cl_1	-0.910	17.910			Cl_1	-0.923	17.923
Pd-O_{Cys}	0.3482	O_{Cys}	-0.765	8.765	Pd-S_{Cys}	0.7147	S_{Cys}	-0.261	16.261
NEC	Pd[core]$5s^{0.28}4d^{8.62}5p^{0.20}5d^{0.01}$				Pd[core]$5s^{0.32}4d^{8.76}5p^{0.29}5d^{0.01}$				
	O_3[core]$2s^{1.65}2p^{4.98}3p^{0.01}$				O_3[core]$2s^{1.64}2p^{5.00}3p^{0.01}$				
	$O_{4"}$[core]$2s^{1.64}2p^{5.08}3p^{0.01}$				$O_{4"}$[core]$2s^{1.64}2p^{5.12}3p^{0.01}$				
	$N_{1"}$[core]$2s^{1.29}2p^{4.17}3p^{0.01}$				$N_{1"}$[core]$2s^{1.30}2p^{4.18}3p^{0.01}4p^{0.01}$				
	Cl_1[core]$3s^{1.99}3p^{5.92}$				Cl_1[core]$3s^{1.98}3p^{5.94}$				
	O_{Cys}[core]$2s^{1.69}2p^{5.06}3p^{0.01}$				S_{Cys}[core]$3s^{1.73}3p^{4.50}3d^{0.01}$				

Table S12. The bond length of the interest, the Wiberg bond indices (WBIs), natural atomic charges (NACs), total natural populations (TNPs, in parentheses), and natural electron (NECs) of selected atoms/ions for *post*-reaction complexes (PoRC) of **C2** compound

O–Cys					HS–Cys				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.3906	Pd	0.672	45.328	Pd-O_3	0.3837	Pd	0.491	45.509

Pd-$S_{4"}$	0.5954	O_3	-0.685	8.685	Pd- $S_{4"}$	0.5868	O_3	-0.685	8.685
Pd-$N_{1"}$	0.5120	$S_{4"}$	0.244	15.756	Pd-$N_{1"}$	0.4752	$S_{4"}$	0.243	15.575
Pd-Cl_1	0.0025	$N_{1"}$	-0.487	7.487	Pd-Cl_1	0.0400	$N_{1"}$	-0.478	7.478
		Cl_1	-0.896	17.896			Cl_1	-0.890	17.889
Pd-O_{Cys}	0.3657	O_{Cys}	-0.749	8.749	Pd-S_{Cys}	0.5179	S_{Cys}	0.197	15.803
NEC	Pd[core]$5s^{0.32}4d^{8.74}5p^{0.26}5d^{0.02}$				Pd[core]$5s^{0.34}4d^{8.85}5p^{0.30}5d^{0.01}$				
	O_3[core]$2s^{1.65}2p^{4.99}3p^{0.01}$				O_3[core]$2s^{1.65}2p^{5.00}3p^{0.01}4p^{0.01}$				
	$S_{4"}$[core]$3s^{1.66}3p^{4.06}3d^{0.02}$				$S_{4"}$[core]$3s^{1.65}3p^{4.08}3d^{0.02}$				
	$N_{1"}$[core]$2s^{1.30}2p^{4.16}3p^{0.02}$				$N_{1"}$[core]$2s^{1.30}2p^{4.15}3p^{0.01}4p^{0.01}$				
	Cl_1[core]$3s^{1.98}3p^{5.91}$				Cl_1[core]$3s^{1.98}3p^{5.91}$				
	O_{Cys}[core]$2s^{1.68}2p^{5.05}3p^{0.01}$				S_{Cys}[core]$3s^{1.65}3p^{4.08}3d^{0.02}$				
O–Cys$^-$					**S–Cys$^-$**				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.3870	Pd	0.668	45.332	Pd-O_3	0.3348	Pd	0.341	45.659
Pd-$S_{4"}$	0.3870	O_3	-0.685	8.685	Pd- $S_{4"}$	0.6038	O_3	-0.699	8.700
Pd-$N_{1"}$	0.5044	$S_{4"}$	0.241	0.241	Pd-$N_{1"}$	0.3939	$S_{4"}$	0.202	15.798
Pd-Cl_1	0.0017	$N_{1"}$	-0.488	7.488	Pd-Cl_1	0.0007	$N_{1"}$	-0.508	7.508
		Cl_1	-0.908	17.908			Cl_1	-0.931	17.931
Pd-O_{Cys}	0.3817	O_{Cys}	-0.758	8.758	Pd-S_{Cys}	0.7497	S_{Cys}	-0.224	16.224
NEC	Pd[core]$5s^{0.32}4d^{8.74}5p^{0.26}5d^{0.01}$				Pd[core]$5s^{0.36}4d^{8.92}5p^{0.37}5d^{0.01}$				
	O_3[core]$2s^{1.65}2p^{4.99}3p^{0.01}$				O_3[core]$2s^{1.65}2p^{5.03}3p^{0.01}$				
	$S_{4"}$[core]$3s^{1.66}3p^{4.06}3d^{0.02}$				$S_{4"}$[core]$3s^{1.64}3p^{4.12}3d^{0.02}$				
	$N_{1"}$[core]$2s^{1.30}2p^{4.16}3p^{0.01}$				$N_{1"}$[core]$2s^{1.30}2p^{4.17}3p^{0.01}$				
	Cl_1[core]$3s^{1.99}3p^{5.92}$				Cl_1[core]$3s^{1.99}3p^{5.94}$				
	O_{Cys}[core]$2s^{1.68}2p^{5.06}3p^{0.01}$				S_{Cys}[core]$3s^{1.72}3p^{4.48}3d^{0.01}$				

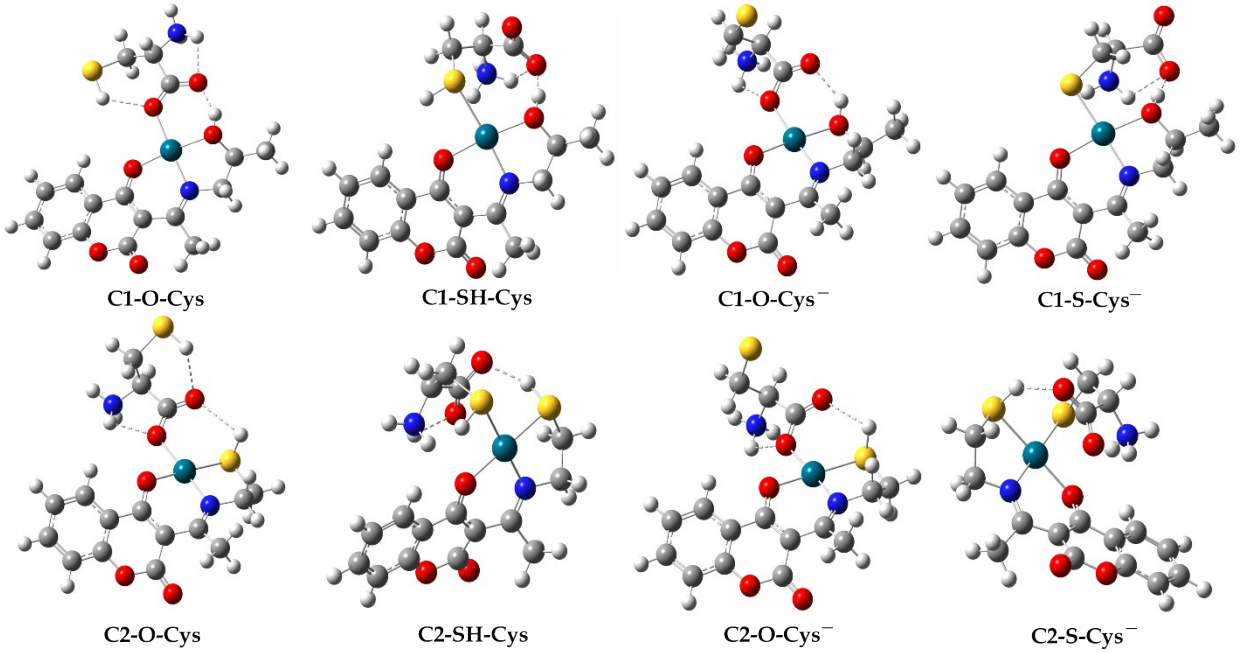

Figure S12. Optimized geometries of products formed in the reaction between the investigated compounds, **C1** and **C2**, and acid-base forms of **L-Cys**/**L-Cys**$^{-}$ with intramolecular hydrogen bond (interrupted line) obtained with M06-2X functional in conjunction with 6–311++G(d,p) basis set C, N, O, Cl, and H/def2-TZVPD, triple-zeta-valence, basis set for atom Pd theory in the water. Legend: grey – carbon atom, white – hydrogen atom, red – oxygen atom, blue – nitrogen atom, yellow – sulfur.

Table S13. The bond length of the interest, the Wiberg bond indices (WBIs), natural atomic charges (NACs), total natural populations (TNPs, in parentheses), and natural electron (NECs) of selected atoms/ions for products of **C1** compound

O–Cys					**HS–Cys**				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.4342	Pd	0.883	45.117	Pd-O_3	0.4409	Pd	0.738	45.262
Pd-$O_{4"}$	0.3211	O_3	-0.647	8.647	Pd-$O_{4"}$	0.3296	O_3	-0.662	8.662
Pd-$N_{1"}$	0.5544	$O_{4"}$	-0.739	8.739	Pd-$N_{1"}$	0.5303	$O_{4"}$	-0.750	8.750
Pd-O_{Cys}	0.3236	$N_{1"}$	-0.479	7.479	Pd-S_{Cys}	0.4618	$N_{1"}$	-0.476	7.476
		O_{Cys}	-0.722	8.724			S_{Cys}	0.131	15.869
NEC	Pd[core]$5s^{0.28}4d^{8.63}5p^{0.20}$ $5d^{0.01}$				Pd[core]$5s^{0.30}4d^{8.71}5p^{0.24}$ $5d^{0.01}$				
	O_3[core]$2s^{1.65}2p^{4.98}3p^{0.01}$				O_3[core]$2s^{1.65}2p^{4.99}3p^{0.01}$				
	$O_{4"}$[core]$2s^{1.65}2p^{5.08}3p^{0.01}$				$O_{4"}$[core]$2s^{1.65}2p^{5.08}3p^{0.01}$				
	$N_{1"}$[core]$2s^{1.29}2p^{4.17}$ $3p^{0.01}$				$N_{1"}$[core]$2s^{1.29}2p^{4.16}3p^{0.01}$				
	O_{Cys}[core] $2s^{1.68}2p^{5.03}3p^{0.01}$				S_{Cys}[core]$3s^{1.67}3p^{4.17}$ $3d^{0.02}$				
O–Cys$^-$					**S–Cys$^-$**				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.4325	Pd	0.882	45.188	Pd-O_3	0.4179	Pd	0.625	45.375
Pd-$O_{4"}$	0.3117	O_3	-0.651	8.651	Pd-$O_{4"}$	0.3238	O_3	-0.656	8.656
Pd-$N_{1"}$	0.5403	$O_{4"}$	-0.733	8.733	Pd-$N_{1"}$	0.4328	$O_{4"}$	-0.769	8.769
Pd-O_{Cys}	0.3401	$N_{1"}$	-0.482	7.482	Pd-S_{Cys}	0.7149	$N_{1"}$	-0.503	7.504
		O_{Cys}	-0.766	8.766			S_{Cys}	-0.245	16.245
NEC	Pd[core]$5s^{0.28}4d^{8.62}$ $5p^{0.20}$ $5d^{0.01}$				Pd[core]$5s^{0.32}4d^{8.76}5p^{0.28}5d^{0.01}$				
	O_3[core]$2s^{1.65}2p^{4.98}3p^{0.01}$				O_3[core]$2s^{1.64}2p^{4.99}$ $3p^{0.01}$				
	$O_{4"}$[core]$2s^{1.64}2p^{5.08}3p^{0.01}$				$O_{4"}$[core]$2s^{1.64}2p^{5.11}3p^{0.01}$				
	$N_{1"}$[core]$2s^{1.29}2p^{4.17}$ $3p^{0.01}$				$N_{1"}$[core]$2s^{1.30}2p^{4.18}4s^{0.01}4p^{0.01}$				
	O_{Cys}[core] $2s^{1.69}2p^{5.06}3p^{0.01}$				S_{Cys}[core]$3s^{1.74}3p^{4.48}3d^{0.01}$				

Table S14. The bond length of the interest, the Wiberg bond indices (WBIs), natural atomic charges (NACs), total natural populations (TNPs, in parentheses), and natural electron (NECs) of selected atoms/ions for products of **C2** compound

O–Cys					HS–Cys				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.3877	Pd	0.677	45.323	Pd-O_3	0.3745	Pd	0.454	45.546
Pd-$S_{4"}$	0.5953	O_3	-0.658	8.658	Pd-$S_{4"}$	0.6359	O_3	-0.739	8.645
Pd-$N_{1"}$	0.5215	$S_{4"}$	0.244	15.756	Pd-$N_{1"}$	0.4870	$S_{4"}$	0.216	15.784
Pd-O_{Cys}	0.3528	$N_{1"}$	-0.482	7.482	Pd-$S_{4"}$	0.5193	$N_{1"}$	-0.484	7.484
		O_{Cys}	-0.748	8.748			S_{Cys}	0.191	15.809
NEC	Pd[core]$5s^{0.32}4d^{8.74}5p^{0.26}5d^{0.01}$				Pd[core]$5s^{0.35}4d^{8.86}5p^{0.32}5d^{0.02}$				
	O_3[core]$2s^{1.65}2p^{4.99}3p^{0.01}$				O_3[core]$2s^{1.65}2p^{5.04}3p^{0.03}$				
	$S_{4"}$[core] $3s^{1.66}3p^{4.06}3d^{0.02}$				$S_{4"}$[core] $3s^{1.64}3p^{4.11}3d^{0.02}$				
	$N_{1"}$[core]$2s^{1.29}2p^{4.17}$ $3p^{0.01}$				$N_{1"}$[core]$2s^{1.30}2p^{4.16}3p^{0.02}$				
	O_{Cys}[core] $2s^{1.68}2p^{5.05}3p^{0.01}$				S_{Cys}[core]$3s^{1.65}3p^{4.13}3d^{0.02}$				
O–Cys$^-$					**S–Cys$^-$**				
Bond	**WBI**	**Atoms**	**NAC**	**TNP**	**Bond**	**WBI**	**Atoms**	**NAC**	**TNP**
Pd-O_3	0.3842	Pd	0.670	45.330	Pd-O_3	0.3446	Pd	0.346	45.654
Pd-$S_{4"}$	0.5962	O_3	-0.656	8.656	Pd-$S_{4"}$	0.6044	O_3	-0.727	8.727
Pd-$N_{1"}$	0.5116	$S_{4"}$	0.246	15.755	Pd-$N_{1"}$	0.3955	$S_{4"}$	0.213	15.787
Pd-O_{Cys}	0.3726	$N_{1"}$	-0.486	7.486	Pd-$S_{4"}$	0.7377	$N_{1"}$	-0.511	7.511
		O_{Cys}	-0.758	8.758			S_{Cys}	-0.217	16.217
NEC	Pd[core]$5s^{0.32}4d^{8.74}5p^{0.26}$ $5d^{0.01}$				Pd[core]$5s^{0.36}4d^{8.92}5p^{0.36}5d^{0.02}$				
	O_3[core]$2s^{1.65}2p^{4.99}3p^{0.01}$				O_3[core]$2s^{1.65}2p^{5.03}3p^{0.01}$				
	$S_{4"}$[core] $3s^{1.66}3p^{4.06}3d^{0.02}$				$S_{4"}$[core] $3s^{1.64}3p^{4.11}3d^{0.02}$				
	$N_{1"}$[core]$2s^{1.30}2p^{4.16}3p^{0.02}$				$N_{1"}$[core]$2s^{1.30}2p^{4.18}3p^{0.01}$				
	O_{Cys}[core] $2s^{1.68}2p^{5.06}3p^{0.01}$				S_{Cys}[core]$3s^{1.72}3p^{4.47}3d^{0.02}$				

Table S15. Calculated values of kinetic parameters: Gibbs activation energy (ΔG_a), reaction rate constants (k), effective values of rate constants (k^{eff}) and the sum of effective values of rate constants ($k^{eff,\,sum}$) [$M^{-1}s^{-1}$] estimated at 288 K and 298 K.

C1	k_{288}	k^{eff}_{288}	$k^{eff,\,sum}_{288}$	Γ_i (%)	k_{298}	k^{eff}_{298}	$k^{eff,\,sum}_{298}$	Γ_i (%)
O–Cys	5.60×10^{3}	4.83×10^{3}	**4.94×10^{4}**	9.8	6.30×10^{3}	5.44×10^{3}	**6.13×10^{4}**	8.9
HS–Cys	9.30×10^{2}	8.03×10^{2}		1.6	1.20×10^{3}	1.04×10^{3}		1.7
O–Cys^{-}	9.90×10^{3}	1.35×10^{3}		2.7	1.10×10^{4}	1.50×10^{3}		2.5
S–Cys^{-}	3.10×10^{5}	4.24×10^{4}		85.8	3.90×10^{5}	5.33×10^{4}		87.0
C2	k_{288}		k^{eff}_{288}		k_{298}		k^{eff}_{298}	
O–Cys	8.80×10^{4}	7.60×10^{4}	**8.16×10^{4}**	93.1	9.70×10^{4}	8.37×10^{4}	**9.01×10^{4}**	92.9
HS–Cys	1.90×10^{3}	1.64×10^{3}		2.0	2.30×10^{3}	1.99×10^{3}		2.2
O–Cys^{-}	3.20×10^{2}	4.38×10^{1}		0.1	4.30×10^{2}	5.88×10^{1}		0.1
S–Cys^{-}	2.90×10^{4}	3.97×10^{3}		4.9	3.20×10^{4}	4.38×10^{3}		4.9

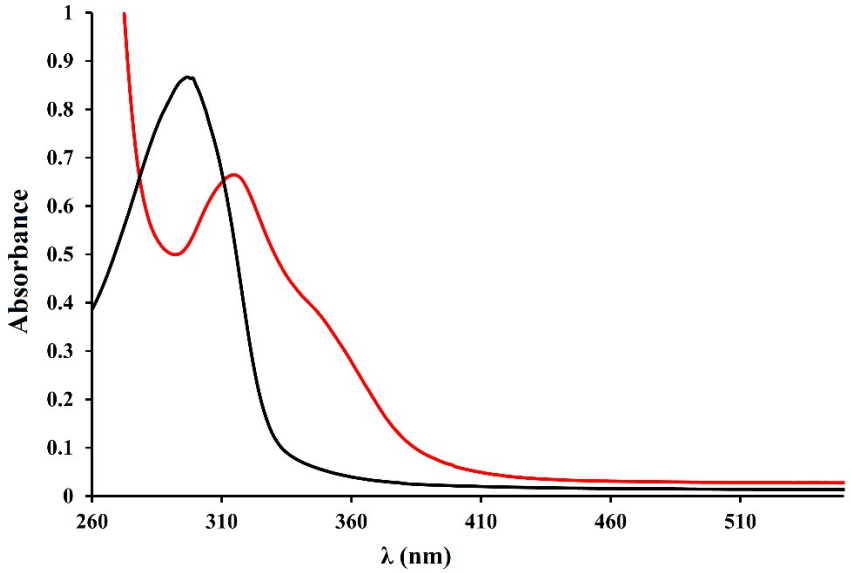

Figure S13. Experimental UV-Vis spectra in Hepes buffer (25 mM Hepes and 50 mM NaCl) of **C1** (red line) and the mixture of **C1** and L-Cys in the ratio 1:1 (black line)

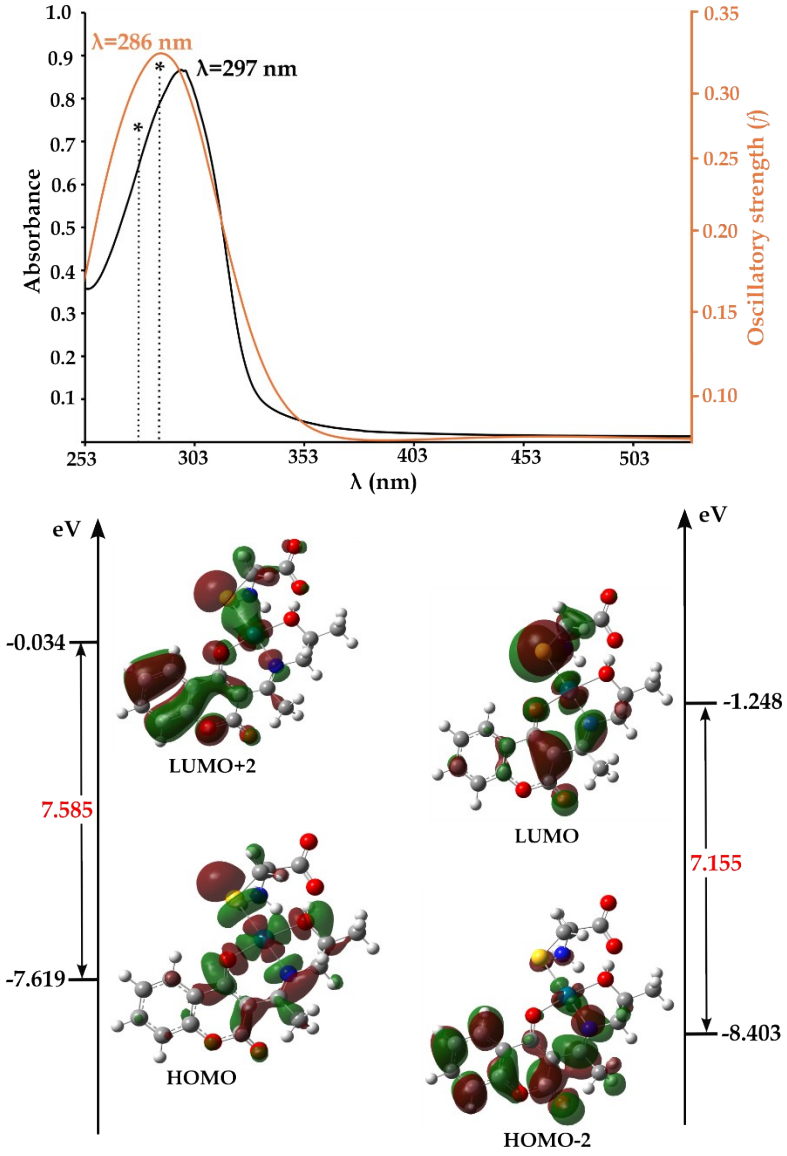

Figure S14. Experimental UV-Vis spectrum in Hepes buffer (25 mM Hepes and 50 mM NaCl) of a 1:1 mixture of **C1** and L-Cys (black line) and simulated spectrum of the **C1-S-Cys**$^{-}$ product (orange line). The HOMO and LUMO orbitals involved in electronic transitions are presented with values of orbital energies (black colour) and energy gap (red colour). The sign "*" and the vertical dashed line represent the oscillator strength value.

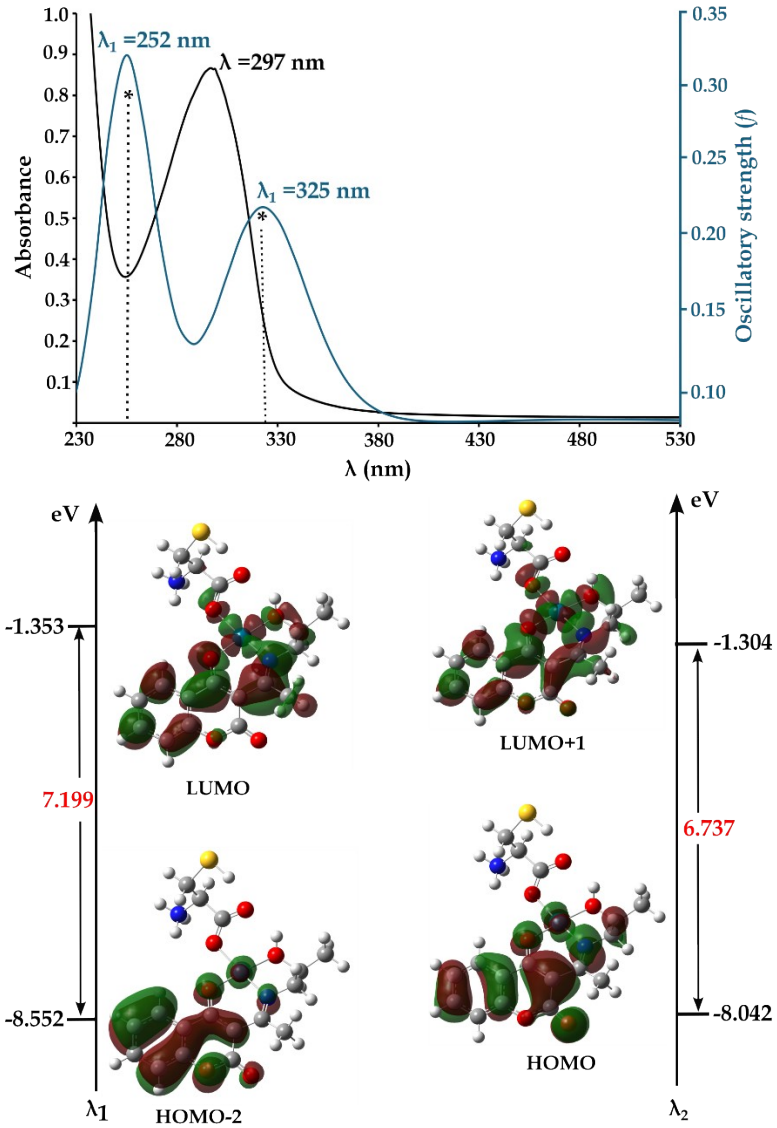

Figure S15. Experimental UV-Vis spectrum in Hepes buffer (25 mM Hepes and 50 mM NaCl) of a 1:1 mixture of **C1** and L-Cys (black line) and simulated spectrum of the **C1-O-Cys** product (blue line). The HOMO and LUMO orbitals involved in electronic transitions are presented with values of orbital energies (black colour) and energy gap (red colour). The sign "*" and the vertical dashed line represent the oscillator strength value.

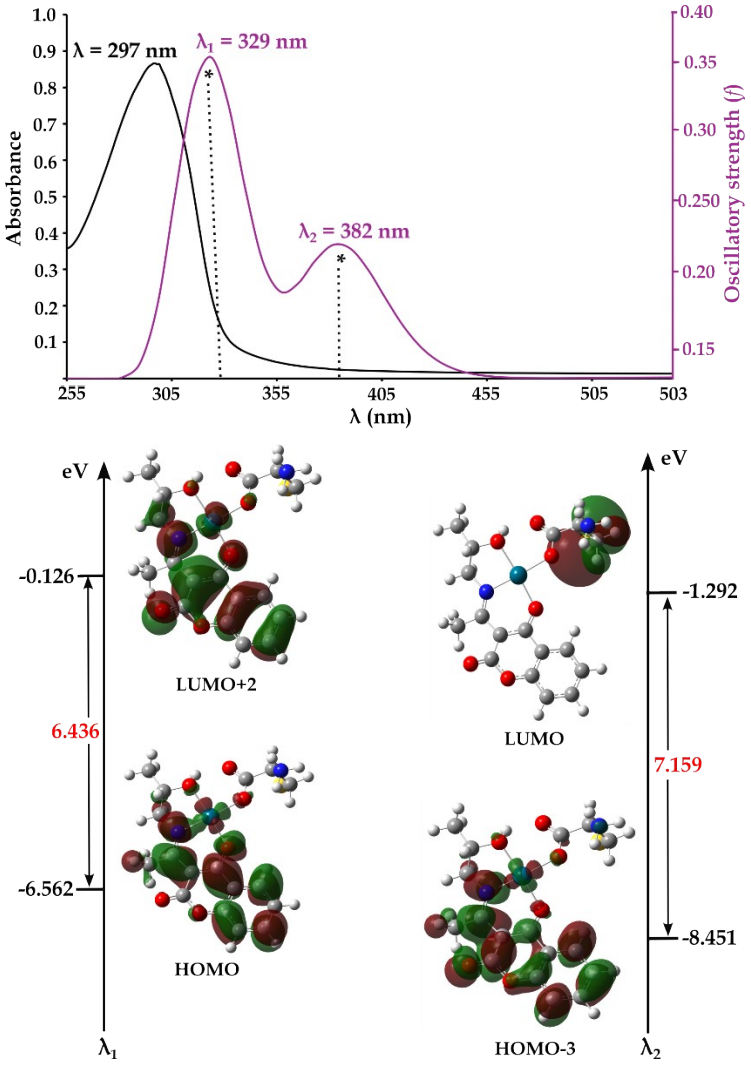

Figure S16. Experimental UV-Vis spectrum in Hepes buffer (25 mM Hepes and 50 mM NaCl) of a 1:1 mixture of **C1** and L-Cys (black line) and simulated spectrum of the **C1-O-Cys**$^{-}$ product (purple line). The HOMO and LUMO orbitals involved in electronic transitions are presented with values of orbital energies (black colour) and energy gap (red colour). The sign "*" and the vertical dashed line represent the oscillator strength value.

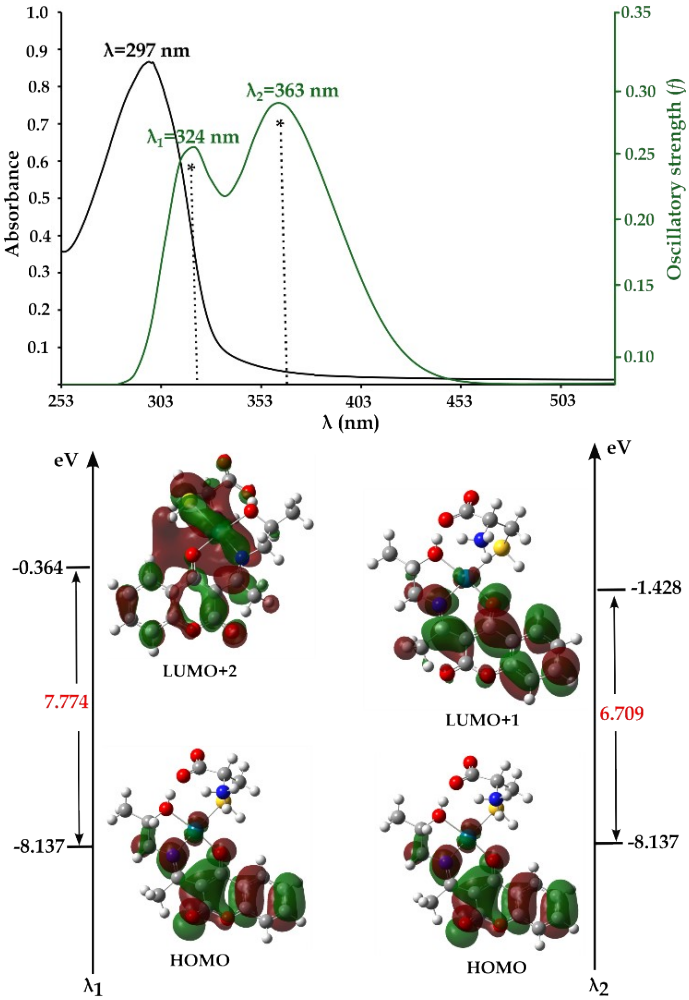

Figure S17. Experimental UV-Vis spectrum in Hepes buffer (25 mM Hepes and 50 mM NaCl) of a 1:1 mixture of **C1** and L-Cys (black line) and simulated spectrum of the **C1-HS-Cys** product (green line). The HOMO and LUMO orbitals involved in electronic transitions are presented with values of orbital energies (black colour) and energy gap (red colour). The sign "*" and the vertical dashed line represent the oscillator strength value.