Zn2+ -Schiff’s base complex acts as the molecular switch “On-Off-On” and a fluorescence probe toward Cu2+ and Ag+ ions

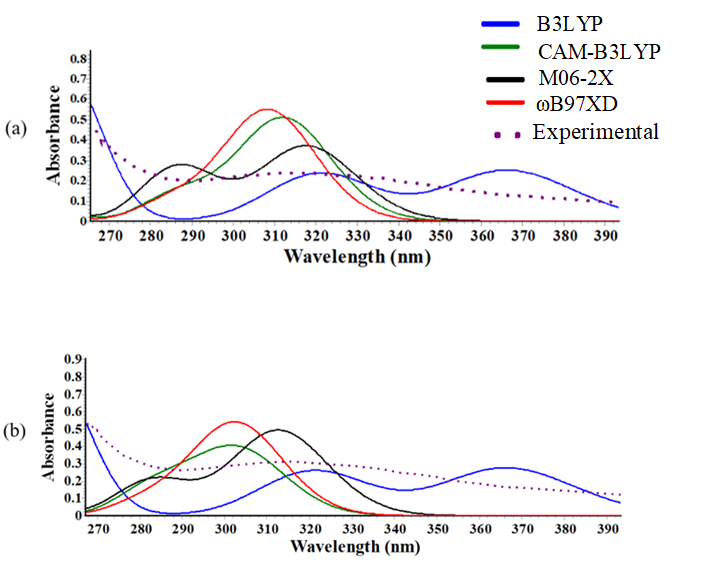
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Table S1: Geometry optimized structures and minimum energies in the gas phase and methanol as a solvent of all the possibilities of the protonation/deprotonation of E-CIS using B3LYP/6-311++G\*\* level of theory.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  |  | Relative energies (kcal/mol) | | |
| E-CIS | Structure | Gas Phase | Solvent Phase (Methanol) | |
| H2L | صورة تحتوي على داخلي, صورة فوتوغرافية, صغير, ولد  تم إنشاء الوصف تلقائياً | 0 | | 0 |
| HL-1 | Chart, bubble chart  Description automatically generated | 325.159 | | 306.852 |
| L-2 | Chart  Description automatically generated | 750.439 | | 615.901 |
| H3L+1 | A picture containing accessory, several  Description automatically generated | -240.587 | | -275.539 |
| H4L+2 | A picture containing indoor, set, several  Description automatically generated | -429.782 | | -547.377 |



**Figure S1:** The simulation of UV-Vis spectra of E-CIS with different TDDFT functionals with 6-311++G\*\* basis set (a) the optimized structure comes from the B3LYP/6-311++G\*\* level of theory. (b) The optimized structures come from the different DFT functionals.

**Table S2:** Natural transition orbitals visualization of E-CIS tautomer emission obtained by using TDDFT/B3LYP/6-311++G\*\* level of theory in the gas-phase and methanol as a solvent.

|  |  |  |  |
| --- | --- | --- | --- |
| Gas Phase | | Methanol | |
| Particle | **Hole** | **Particle** | **Hole** |
| (λ= 451.560 nm) | | (λ= 497.631 nm) | |
|  |  |  |  |
| (λ= 440.318 nm) | | (λ= 455.475 nm) | |
|  |  |  |  |

**Table S3:** Selected bond lengths (Ǻ) and bond angles (°) of E-CIS and K-CIS tautomers in S0 and S1 states obtained by using DFT/TDDFT/B3LYP/6-311++G\*\* levels of theory

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | Gas-phase | | | | Methanol | | | |
|  | **E-CIS** | | **K-CIS** | | **E-CIS** | | **K-CIS** | |
|  | **S0** | **S1** | **S0** | **S1** | **S0** | **S1** | **S0** | **S1** |
| O47–H48 | 0.993 | 0.990 | 1.685 | 1.699 | 0.998 | 0.995 | 1.750 | 1.756 |
| H48–N20 | 1.745 | 1.761 | 1.045 | 1.043 | 1.716 | 1.732 | 1.037 | 1.036 |
| N20–C22 | 1.284 | 1.285 | 1.329 | 1.327 | 1.285 | 1.285 | 1.322 | 1.321 |
| C22–C24 | 1.452 | 1.45 | 1.396 | 1.398 | 1.454 | 1.453 | 1.404 | 1.405 |
| C24–C25 | 1.419 | 1.419 | 1.466 | 1.466 | 1.418 | 1.418 | 1.459 | 1.459 |
| C25–O47 | 1.341 | 1.342 | 1.262 | 1.262 | 1.384 | 1.348 | 1.272 | 1.273 |
| O47–H48–N20 | 147.39 | 146.83 | 140.17 | 139.74 | 148.34 | 147.60 | 138.07 | 138.00 |

***Table S4:*** *Optimized structures and Binding energy/kcal/mol for the studied complexes using B3LYP/LANL2DZ/6-311++G\*\* level of theory in the gas phase and methanol*

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **A picture containing pool ball  Description automatically generated** | | |  | | |
| **Complex** | **Symbol** | **Optimized structure** | **Gas Phase** | **Methanol** | **water** |
| [Zn2L2]0 | **1** | Chart, bubble chart  Description automatically generated | -886.686 | -210.952 | -172.059 |
| [Cu2L2]0. H2O | **2S** | Chart  Description automatically generated | -954.698 | -2.707 | -410.133 |
| [Cu2L2]0. H2O | **2T** | Chart, bubble chart  Description automatically generated | -986.647 | -33.719 | -438.747 |
| [Ag2L2]0 | **3** | Chart, bubble chart  Description automatically generated | -27.399 | 327.961 | -82.615 |
| [AgZnL2]-1. H2O | **4** | Chart, bubble chart  Description automatically generated | -467.373 | 283.409 | -129.389 |
| [CuZnL2]0 | **5** | Chart, bubble chart  Description automatically generated | -943.543 | 79.807 | -302.893 |
| [AgCuL2]-1 | **6** | Chart, bubble chart  Description automatically generated | -539.838 | 134.357 | -262.858 |
| [Zn2L2]0. [Ag+]2 (S) | **7S** | Chart, bubble chart  Description automatically generated | -971.876 | 202.352 | -170.553 |
| [Zn2L2]0. [Cu+2] | **8D** | Chart, bubble chart  Description automatically generated | -969.017 | -142.191 | -121.043 |
| [Zn2L2]0. [Cu+2] | **8U** | A picture containing indoor, set, several, arranged  Description automatically generated | -1263.477 | 76.666 | -291.567 |
| [Zn2L2]0. [Cu+2]2 (T) | **9T** | Chart, scatter chart  Description automatically generated | -1254.250 | 71.540 | -306.244 |

**Table S5:** Optimized geometric parameters of L-2 ligand and metal complexes obtained by using DFT/B3LYP/LANL2DZ/6-311++G\*\* level of theory (bond lengths in Å and bond angles in degrees).

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Bond Parameters | L-2 | Zinc complexes | | | | | Copper complexes | |
| 1 | | 7 | 8D | 8T | 2S / 2T | |
| L-2  O47-C25  N20=C22  O47-C25-C24  N20=C22-C24 | Theoretical | Theoretical | Exp. | Theoretical | | | Theoretical | Exp. |
| 1.250 | 1.320 | - | 1.320 | 1.31 | 1.32 | 1.32 / 1.32 | - |
| 1.280 | 1.320 | - | 1.330 | 1.31 | 1.32 | 1.31 / 1.31 | - |
| 124.8 | 122.73 | - | 122.34 | 122.19 | 122.05 | 121.5 / 121.05 | - |
| 128.9 | 128.15 | - | 129.29 | 128.58 | 128.11 | 128.46 / 128.75 | - |
| Zn1-Zn31  N3-Zn1  O5-Zn1  N3-(Ag97 or Cu97)  N3-(Ag98 or Cu97)  O5-M-N3  O5-M-N2  N2-Zn1-N3  O5-Zn1-O6  Ag97-N3-Ag98  N2-(Ag97 or Cu97)-N3 | - | 6.722 | 7.141 | 5.73 | 5.48 | 6.67 | 6.89 / 6.90 | -- |
| - | 2.091 | 2.016 | 2.09 | 2.08 | 2.09 | 2.051 / 2.065 | 1.955 |
| - | 1.981 | 1.907 | 1.93 | 1.98 | 1.97 | 1.972 / 1.947 | 1.965 |
| - | - | - | 4.22 | - | 4.12 | - | - |
| - | - | - | 4.66 | 4.55 | - | - | - |
| - | 89.80 | 96.07 | 92.79 | 90.87 | 89.55 | 87.25 / 86.16 | 94.30 |
| - | 127.76 | 122.55 | 113.89 | 114.88 | 128.38 | 143.51 / 156.80 | 141.90 |
| - | 122.58 | 111.73 | 134.88 | 134.15 | 123.76 | 115.25 / 110.59 | 104.00 |
| - | 103.62 | 108.44 | 111.37 | 108.44 | 101.25 | 89.92 / 86.3 | 90.70 |
| - | - | - | 87.73 | - | - | - | - |
| - | - | - | 53.01 | 54.12 | 52.34 | - | - |

**Table S6**. Energies of HOMOs , LUMOs and Eg=LUMO-HOMO are calcualted using DFT/B3LYP/LANL2DZ/6-311++G\*\* level of theory in the gas-phase.

|  |  |  |  |
| --- | --- | --- | --- |
|  | HOMO | LUMO | Eg |
| ECIS | -6.023 | -1.961 | 4.062 |
| L-2 | 0.509 | 3.641 | 3.132 |
| 1 | -5.616 | -2.029 | 3.587 |
| 2S | -4.699 | -4.252 | 0.447 |
| 2T | -5.541 | -1.963 | 3.578 |
| 3 | -0.289 | 3.052 | 3.341 |
| 4 | -2.149 | -0.085 | 2.064 |
| 5 | -5.612 | -2.017 | 3.595 |
| 6 | -2.2 | -0.008 | 2.192 |
| 7 | -10.111 | -7.616 | 2.495 |
| 8D | -10.832 | -7.128 | 3.704 |
| 8U | -10.518 | -7.249 | 3.269 |
| 9T | -15.312 | -12.331 | 2.981 |
| 9S | -15.357 | -15.045 | 0.312 |

**Table S7:** Electronic absorption energy (nm/eV), corresponding oscillator strengths, assignments and coefficients of the ligand and its complexes obtained by using TDDFT/B3LYP/LANL2DZ/6-311++G\*\* level of theory.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Compound | Exp. λ (nm) | λ (nm) |  | f | Assignment | Coefﬁcient |
| E-CIS | 314 | 314.467 | 3.943 | 0.033 | H→L | 0.52 |
| 258 | 257.460 | 4.816 | 0.148 | H-4→L | 0.59 |
| 1 | 398 | 396.358 | 3.128 | 0.099 | H→L+1 | 0.48 |
| 278 | 275.559 | 4.499 | 0.012 | H-1→L+4 | 0.53 |
| 2S | 325  274 | 328.995 | 3.769 | 0.002 | H-4→L+4 | 0.62 |
| 275.326 | 4.503 | 0.002 | H-3→L | 0.42 |
| 2T | 326.585 | 3.796 | 0.005 | H-5α→L+1α | 0.45 |
| 276.585 | 4.483 | 0.009 | H-7ꞵ→ L+4ꞵ | 0.55 |
| 7 | 323 | 322.290 | 3.847 | 0.066 | H-10→L | 0.31 |
| 278 | 278.493 | 4.452 | 0.023 | H-6→ L+4 | 0.38 |
| 8D | 357  281 | 356.278 | 3.480 | 0.001 | Lꞵ→ H-2ꞵ | 0.96 |
| 286.863 | 4.322 | 0.004 | L+1ꞵ →H-10ꞵ | 0.52 |
| 8U | 359.606 | 3.448 | 0.000 | L+2α →H-3α | 0.38 |
| 292.121 | 4.244 | 0.005 | Lꞵ→ H-3ꞵ | 0.82 |

**Table S8:** Natural transition orbitals (NTO) visualization of complexes in gas-phase and solution (methanol) obtained by using TDDFT/B3LYP/ LANL2DZ /6-311++G\*\* method

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Complex | Absorptions in the gas-phase | | | Absorptions in solution (Methanol) | |
| **Hole** | **Particle** | | **Hole** | **particle** |
| 1 | (λ= 396.358nm) n | | | (λ= 387.120nm) n | |
|  | |  |  |  |
| (λ= 275.559nm) | | | (λ= 285.950nm) | |
|  |  | |  |  |
| 7 | (λ= 322.290 nm) n | | | (λ= 325.061 nm) n | |
|  |  | |  |  |
| (λ= 278.493 nm) | | | (λ= 278.199 nm) | |
|  |  | |  |  |
| 8D | (λ= 356.278 nm) n | | | (λ= 358.815 nm) n | |
|  |  | |  |  |
| (λ= 286.863 nm) | | | (λ= 288.989 nm) | |
|  |  | |  |  |