SUPPORTING INFORMATION.

Structural characterization of a fluorescein hydrazone molecular switch with application towards logic gates†

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1. Synthesis

1.1. Synthesis of Fluorescein hydrazone (2)

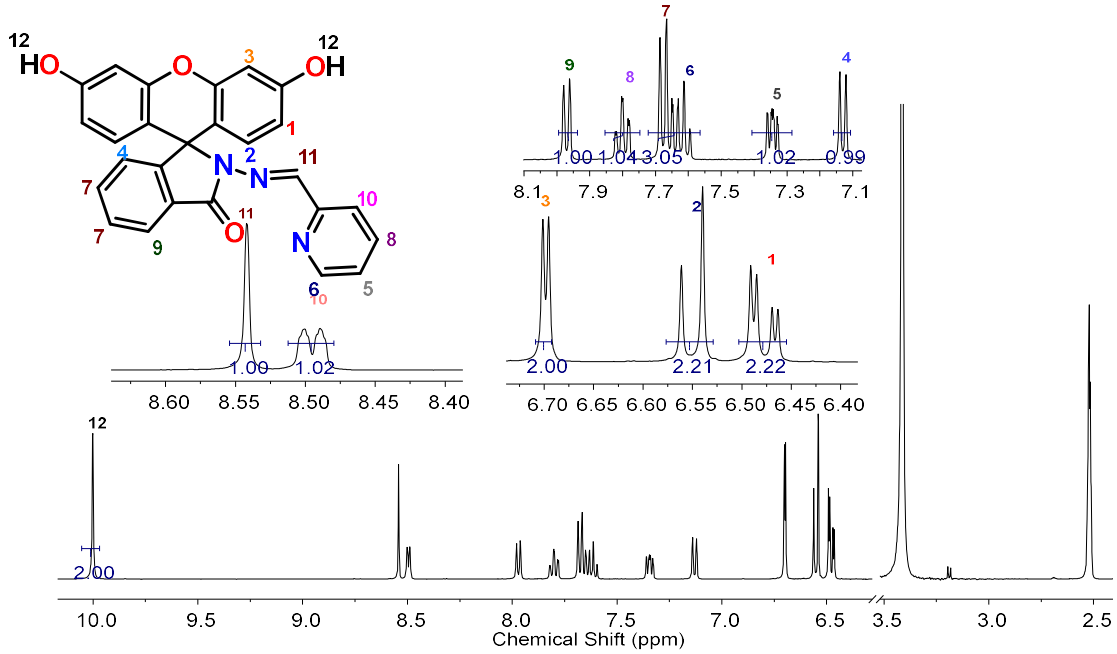

Figure S 1. ^{1}H NMR spectrum of **2** in DMSO- d6 at 400 MHz..

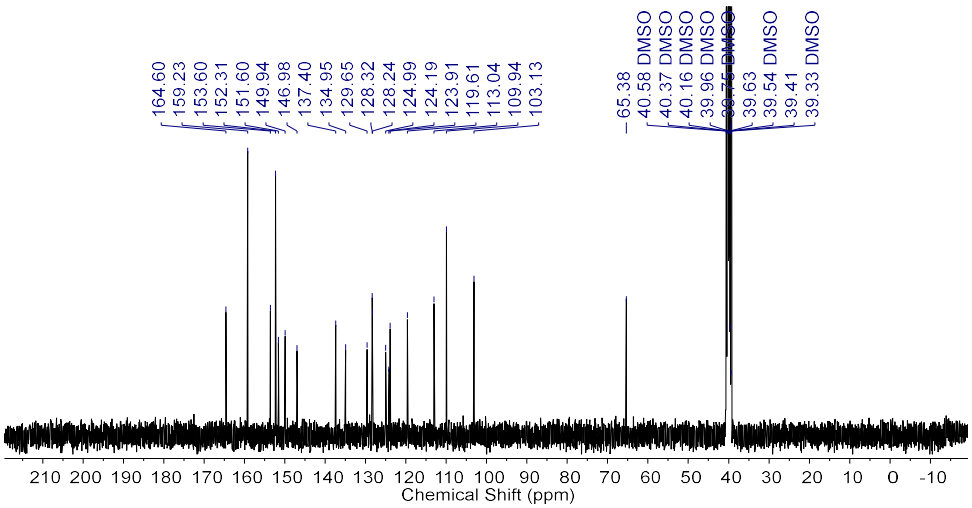

Figure S 2. ^{13}C NMR spectrum of **2** in DMSO d6 at 101 MHz.

1.1.1. Crystallographic Data of fluorescein hydrazone (2).

Table S 1. Crystallographic data and refinement parameters for fluorescein hydrazone (2).

Compound	fluorescein-hydrazone
Empirical Formula	$C_{23}H_{16}N_3O_4$, $C_{23}H_{16}N_3O_4$, H_2O
FW ($g \cdot mol^{-1}$)	887.86
Temp. (K)	293
Crystal system	Triclinic
Space Group	Pī
Unit cell	
***a* (Å)**	9.9987(18)
***b* (Å)**	14.262(2)
***c* (Å)**	15.699(2)
α (°)	97.420(12)
β (°)	97.333(16)
γ (°)	108.183(16)
Volume ($Å^3$)	2075.3(6)
Z	4
ρ calcd ($mg \cdot m^{-3}$)	1.423
Abs.Coeff (mm^{-1})	0.099
F(000)	924
θ range (°)	2.7 to 27.1
Reflections collected /	9136/9136
Unique [R(int)]	[0.128]
Completeness (%)	99
Data / restraints	9136/0/638
/ parameters	
Gof on F^2	1.03
R1 [I>2σ(I)]	0.1139
wR2[I>2σ(I)]	0.3660

1.2. M^{2+} metal complex preparation.

1.2.1. 2-Zn

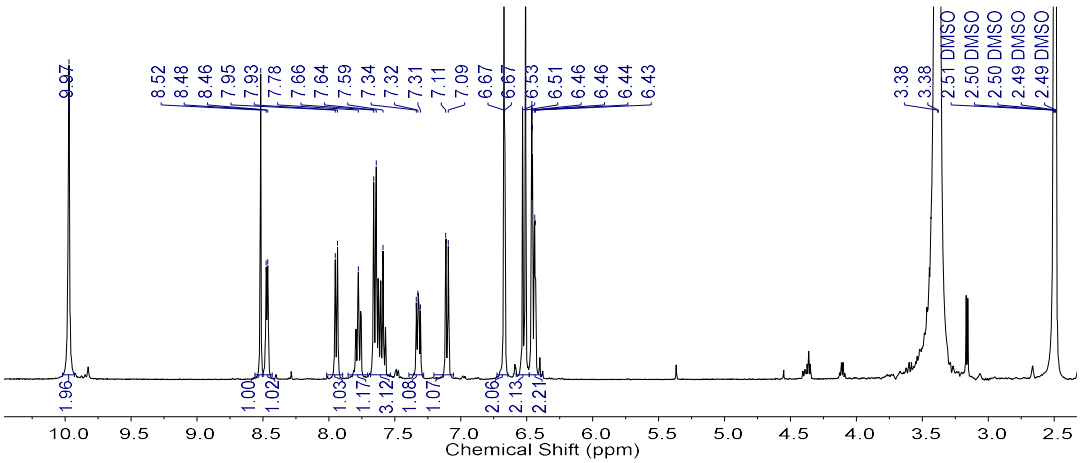

Figure S 3. ^{1}H NMR spectrum of 2-Zn in DMSO-d_6 at 400 MHz.

1.2.2. 2-Ni

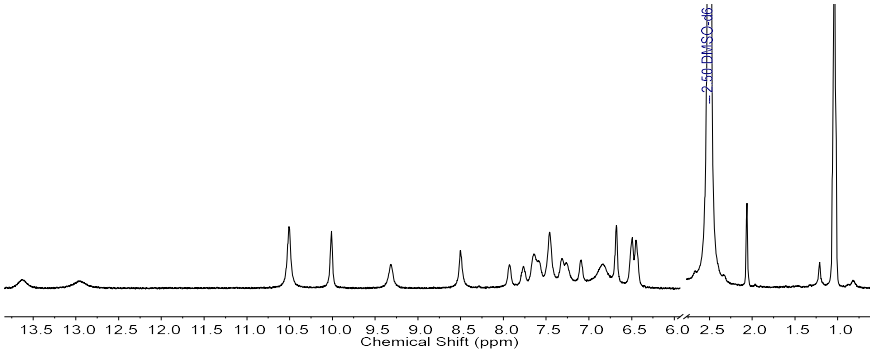

Figure S 4. ^{1}H NMR spectrum of 2-Ni in DMSO-d_6 at 400 MHz.

1.2.3. 2Cu

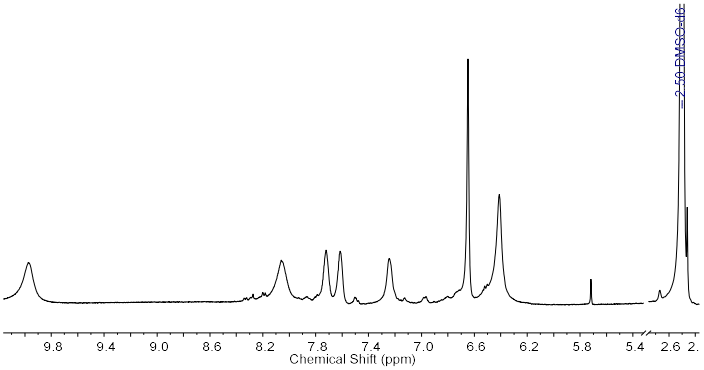

Figure S 5.^{1}H NMR spectrum of 2-Cu in DMSO-d_6 at 400 MHz.

2. Electrochemical Characterization

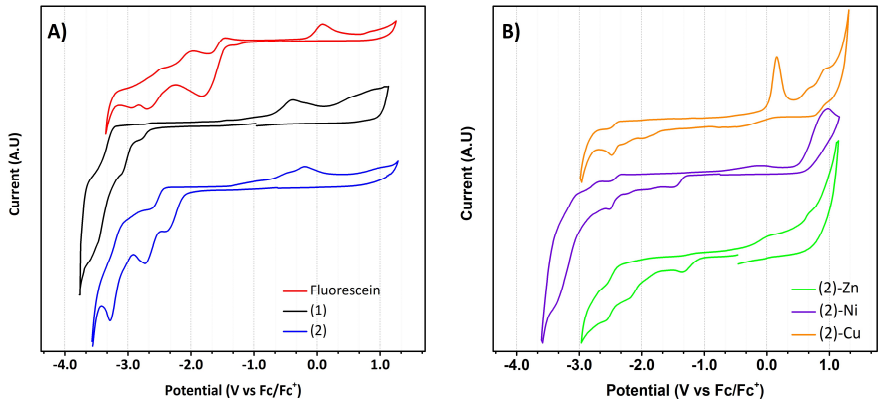

Figure S 6. (A) full CV of Fluorescein, and derivatives (1) and (2). (B) Full CV of Complexes of Zn^{2+}, Ni^{2+}, Cu^{2+} with Acylhidrazone (2).

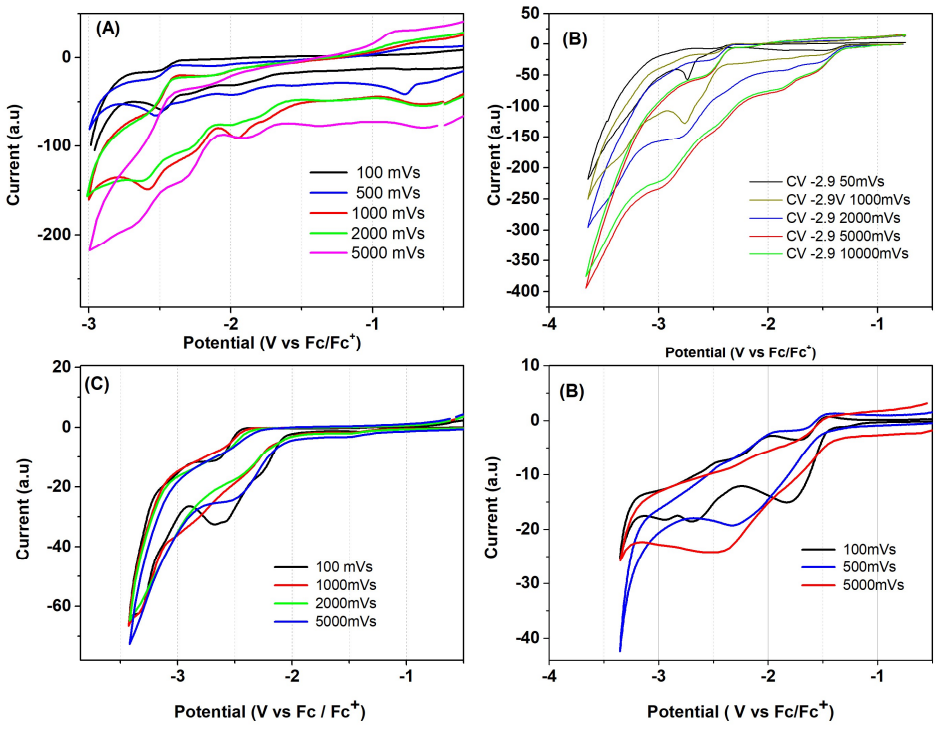

Figure S 7. (A) CVs at different Scan rates of **2-Cu**. (B) CVs at different Scan rates of **2-Ni**. (C) CVs at different Scan rates of Compound **2**. (D) (A) CVs at different Scan rates of Fluorescein

3. Spectroscopic Characterization.

Acid Base Titrations.

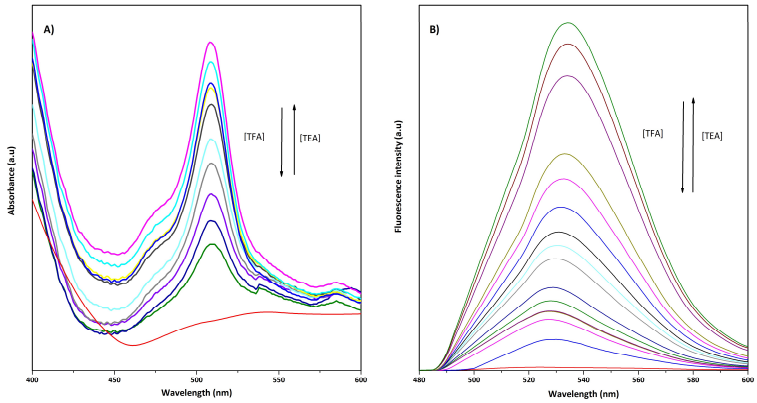

Figure S 8. UV-Visible spectra (A) and Fluorescence titration spectra (B) of compound **2 (**50 µM) upon the addition of trimethylamine (TEA) and Trifluoroacetic acid(TFA) on ethanol.

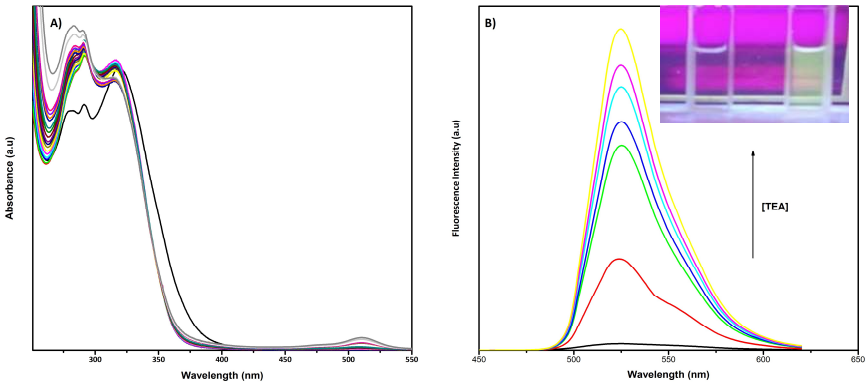

Figure S 9 UV-Visible spectra (A) and Fluorescence titration spectra (B) of compound **2-Zn (**50 µM) upon the addition of trimethylamine (TEA). Onset : **2-zn** before and after the addition of TEA

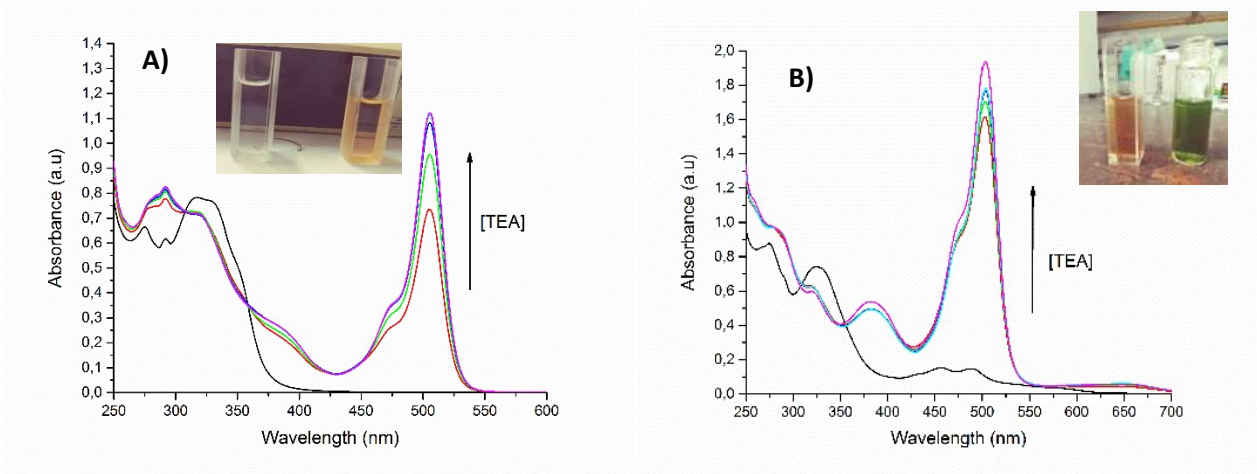

Figure S 10 UV-Visible spectra of (A) compound **2-Ni (**50 µM) upon the addition of trimethylamine (TEA) Onset: **2-Ni** before and after the addition of TEA. (B) compound **2-Cu** (50 µM) upon the addition of trimethylamine (TEA) Onset : **2-Cu** before and after the addition of TEA

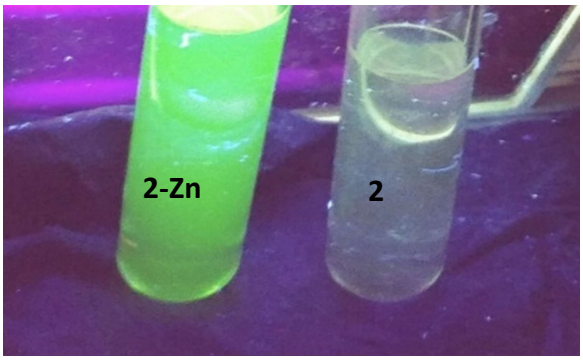

Figure S 11. Comparison of both **2-Zn** complex and acylhidrazone **2** on basic media.

Quantum Yield Calculations.

Quantum yield of all compounds were measured using a NaOH 0,1N using the slope comparative method using 490 nm as excitation wavelength for the emission data and a solution of fluorescein as Standard all the data its summary in the Table S 2

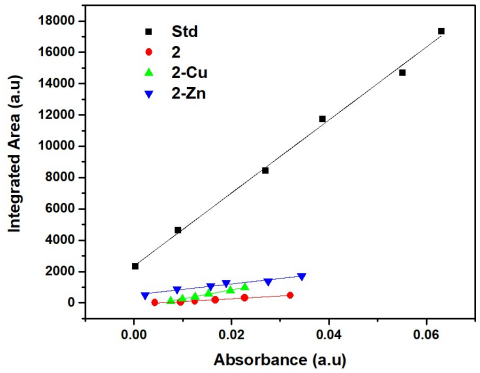

Figure S 12. Linearization of Quantum yield data for compounds **2**, **2-Cu** and **2-Zn**

Table S 2 Linearization data of quantum yield measures.

Plot	Fluorescein (Std)	(4)	(4)Cu	4(Zn)
Intercept	2358.02032 ± 262.55487	-99.67836 ± 17.33	-309.42697 ± 25.23	508.82688 ± 63.03529
Slope	233051.59073 ± 6659.81189	17842.69129 ± 928.38	56858.21996 ± 1622.043	34867.49695 ± 3013.06635
r	0.99837	0.99463	0.99838	0.98539

Table S3. Quantum Yield of the Complexes of hydrazone 2

Compound	Solvent (25°C)	Quantum Yield
Fluorescein	NaOH 0,1N at °C	0,89[1]
1	0.02 at Buffer Tris HCl Buffer 25 °C	0,02[2]
2	Ethanolic NaOH 0,1N	0,07
2-Zn	Ethanolic NaOH 0,1N	0,15
2-Cu	Ethanol	0,26

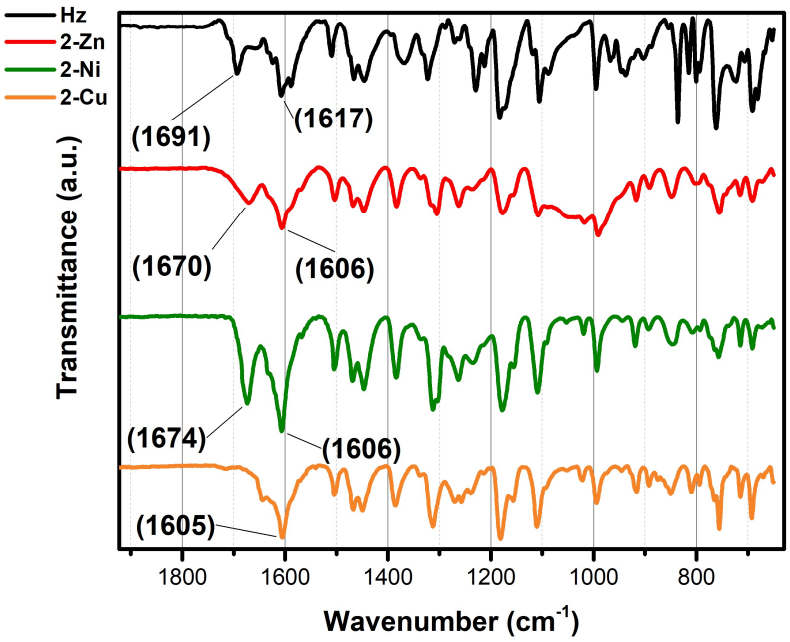

Figure S 13. Partial FT-IR of 2, 2-Ni, 2-Zn and 2-Cu.

4. References.

1 C. Würth, M. Grabolle, J. Pauli, M. Spieles and U. Resch-Genger, *Nat. Protoc.*, 2013, **8**, 1535–1550.

2 S.-Q. Wu, Q.-W. Xie, G.-Y. An, X. Chen, C.-M. Liu, A.-L. Cui and H.-Z. Kou, *Dalton Trans.*, 2013, **42**, 4369–72.