Electronic Supplementary Material (ESI) for Chemical Communications

A pyrene based fluorescent sensor for Zn^{2+} ions: A molecular 'butterfly'

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Supplementary Material:

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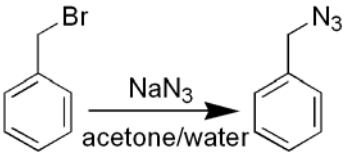
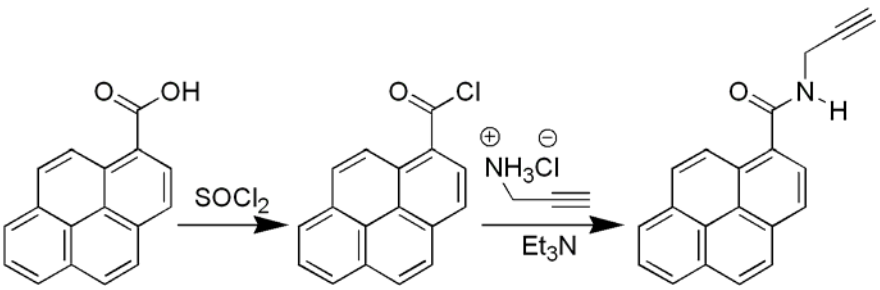
General techniques: $^{1}H/^{13}C$ and 2D NMR spectra were recorded on a Bruker Ultrashield plus 400 MHz spectrometer in the appropriate deuterated solvents. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (0 ppm) as the internal standard and coupling constants (*J*) are recorded in hertz (Hz). The multiplicities in the ^{1}H NMR spectra are reported as (br) broad, (s) singlet, (d) doublet, (dd) doublet of doublets, (ddd) doublet of doublet of doublets, (t) triplet, (sp) septet and (m) multiplet. All spectra are recorded at ambient temperature. UV-Vis experiments were performed on a Beckman DU-70 UV-Vis spectrometer. Low resolution mass spectra were measured with Finnigan TSQ70 and VG Analytical ZAB2-E instruments. IR spectra were recorded on a Nicolet Nexus 470 FT-IR paired with a Smart Orbit ATR attachment. The characteristic functional groups are reported in wavenumbers (cm^{-1}), and are described as weak (w), medium (m), strong (s) and very strong (vs). Fluorescence experiments were carried out on a QuantaMaster™ 40 Intensity Based spectrofluorometer from PTI technologies in the steady-state; slitwidths 0.50 mm; λ_{Ex} = 340 nm λ_{Em} = 360 nm to 600 nm. Elemental analysis was carried out at Atlantic Microlab Inc.

Synthesis:

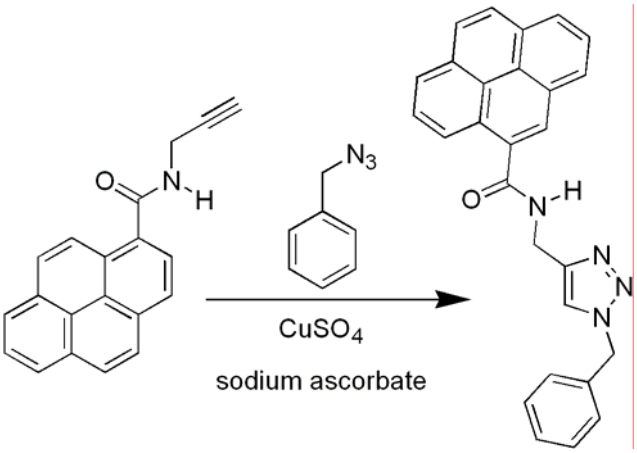


Preparation of azidomethylbenzene[1]: Bromomethylbenzene (1.44 g, 8.40 mmol) and sodium azide (1.04 g, 16.00 mmol) were dissolved in a 3:1 mixture of acetone and water (30 mL) and stirred at room temperature for 2 h. A mixture of dichloromethane (25 mL) and water (25 mL) was then added to the reaction and stirred for 10 mins. The organic layer was separated and washed three times with water (50 mL), dried over magnesium sulfate, filtered and the solvent removed to produce a yellowish oil. The oil was then subjected to column chromatography on silica (40-63 μm, 60 Å) using hexane and ethyl acetate as the eluent (80:20) to produce the desired diazidexylene as an oil (1.00 g, 7.50 mmol, 89%). Spectroscopic data agreed with the published procedure. ^{1}H NMR ($CDCl_3$ *J*/*Hz* δ/ppm); δ 7.26-7.40 (m, 5H, CH_{Ar}), 4.30 (s, 2H, CH_2); IR (ATR solid); 3000, ν_{C-H} (w), 2089 $\nu_{N\equiv N}$ (vs), cm^{-1}.



Preparation of N-prop-2-ynylpyrene (1); adapted from ref [2]: 1-Pyrenecarboxylic acid (138 mg, 0.56 mmol) was dissolved in thionyl chloride (8 mL) and refluxed under argon for 2 h. Excess thionyl chloride was removed under reduced pressure to form a yellow solid which was redissolved in chloroform (50 mL) to which triethylamine (82 μL, 0.59 mmol) and propargylamine (71 μL, 1.28 mmol) were added drop wise at 0 °C and stirred for 1 h. The reaction was allowed to warm to room temperature and left to react for a further 18 h. A saturated solution of brine (50 mL) was then added to the reaction mixture which was subsequently extracted with chloroform (3 × 15 mL). The organic layers were combined and washed with brine (2 × 25 mL) and water (2 × 25 mL), dried over magnesium sulfate, filtered and the solvent was removed under reduced pressure. Column chromatography was carried out using silica (40-63 μm, 60 Å) and ethyl

acetate in hexane as the eluent (15:75). The compound was obtained as a pure yellow solid, (95 mg, 0.33 mmol, 60%); m.p. 181 °C: ^{1}H NMR ^{1}H NMR ($CDCl_3$, 400MHz): δ 8.53 (*d*, 1H, *J* = 10 Hz, CH_{py}), 8.19 (*s*, 1H, CH_{py}), 8.10 (s, 1H, CH_{py}), 8.00-8.10 (m, 6H, CH_{py}), 6.40 (s,1H, NH), 4.42 (m, 2H,CH_2), 2.32 (m,1H,CH); ^{13}C NMR ($CDCl_3$, 400MHz): δ 169.5, 132.7, 131.1, 130.6, 129.8, 128.8, 128.7, 127.0, 126.4, 125.9, 125.8, 124.6, 124.3, 124.2, 124.2, 79.5, 72.0, 30.0; IR (ATR solid) 3278 $\nu_{C\equiv H}$ (vs), 3198 ν_{N-H} (m), 2921, 2855, ν_{C-H} (m), 2070 $\nu_{C\equiv C}$ (w), 1618 $\nu_{C=O}$ amide I (s) 1600 $\delta_{N-H}\nu_{C=O}$ amide II (m) cm^{-1}.



Preparation of compound (3). Compound **1** (100 mg, 0.34 mmol), azidomethyl benzene (46 mg, 0.34 mmol), copper(II)sulfate (20 mg, 0.08 mmol) and sodium ascorbate (67 mg, 0.34 mmol) were dissolved in a 75% acetone/water solution (20 mL) and stirred at room temperature for 48 h. The reaction mixture was then poured into ice cold water (20 mL), where a precipitate formed. The solid was filtered, washed with water (25 mL) and recrystalised from CH_3CN, filtered and dried (70 mg, 0.17 mmol, 50%). m.p. 200 °C: ^{1}HNMR ($CDCl_3$, 400MHz): δ 8.52 (*d*, 1H, *J* = 9 Hz, CH_{py}), 8.22 (d,1H, *J* =3 Hz, CH_{py}), 8.20 (d,1H, *J*=4 Hz, CH_{py}), 8.00-8.12 (m, 6H,CH_{py}), 7.68 (s,1H,$CH_{triazole}$), 7.38-7.40 (m, 3H,CH_{Ar}), 7.28-7.32 (m, 2H,CH_{Ar}), 6.99 (s, 1H,NH), 5.55 (s, 2H,CH_2C_{Ar}), 4.86 (d, 2H, *J* = 5Hz, CH_2N_{amide}); ^{13}C NMR ($CDCl_3$, 400MHz): δ 170.0, 134.5, 132.7, 131.1, 130.6, 130.2, 129.2, 128.8, 128.7, 128.1, 127.1, 126.3, 125.8, 125.7, 124.7, 124.3, 124.3, 122.4, 54.3, 35.7. ESI-MS m/z $[M + H]^+$ = 417; IR (ATR solid); 3243 ν_{N-H} (m), 3129 $\nu_{C\equiv H}$ (m), 3034, 3962, ν_{C-H} (m), 1640 amide I stretch (s) 1596 amide II stretch (m) cm^{-1}; Anal. Calcd for $C_{27}H_{20}N_4O$: H, 4.84; N, 13.45; C, 77.87% Anal Recalcd for $C_{27}H_{20}N_4O.0.5CH_3CO_2CH_2CH_3$; H, 5.25; N, 12.15; C, 75.63%; Found for $C_{27}H_{20}N_4O.0.5\ CH_3CO_2CH_2CH_3$; H, 4.77; N, 12.70; C, 75.43%.

UV-Vis experiments: A stock solution (6.5×10^{-4} M) of compound **3** was prepared by dissolving 2.7 mg in 10 mL of CH_3CN, and then 1 mL was transferred to the UV-Vis cell. From the stock solution eight dilute solutions ranging from 1.5×10^{-5} to 8.0×10^{-5} M were prepared and the UV-Vis spectra were recorded for each sample.

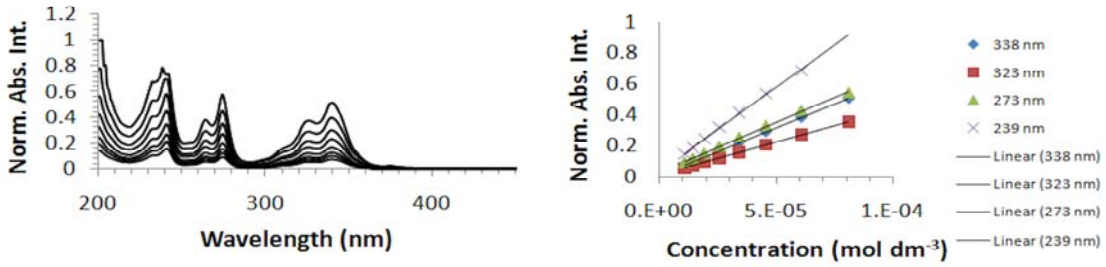
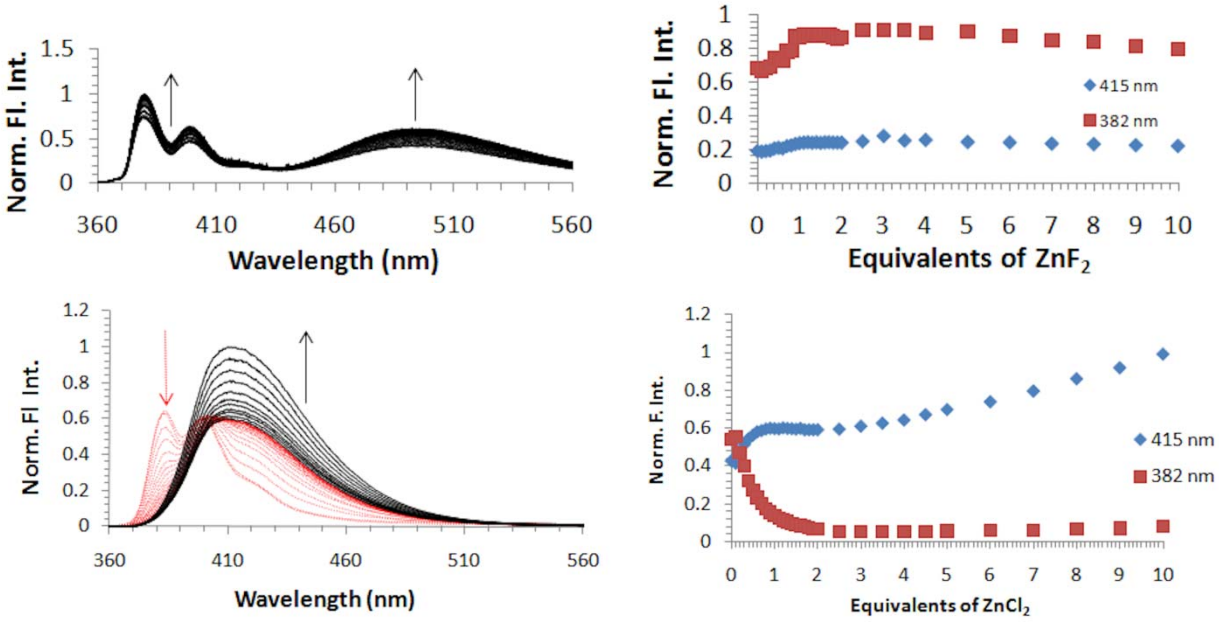


Figure S1: Molar absorptivity of compound **3** at various wavelengths: 338 nm (ε = 6087 M^{-1} cm^{-1}), 323 nm (ε = 6087 M^{-1} cm^{-1}), 273 nm (ε = 6487 M^{-1} cm-^{1}) and 239 nm (ε = 10851 M^{-1} cm^{-1}).

Fluorescence experiments: A stock solution (6.48×10^{-4} M) of compound **3** was prepared in CH_3CN. The solution was excited at λ= 355 nm and scanned from λ 360-600 nm with slit widths set to 0.5 mm. A 10 times more concentrated solution of the Zn^{2+} salt was prepared in CH_3CN and 10 μL (10 μL = 0.1 equivalent of metal salt) aliquots were added to compound **3**; fluorescence spectra were recorded after each addition. Dilution factors were taken into consideration upon binding study determination. The binding constants were determined from fluorescence titrations using HypSpec 2006.[3]



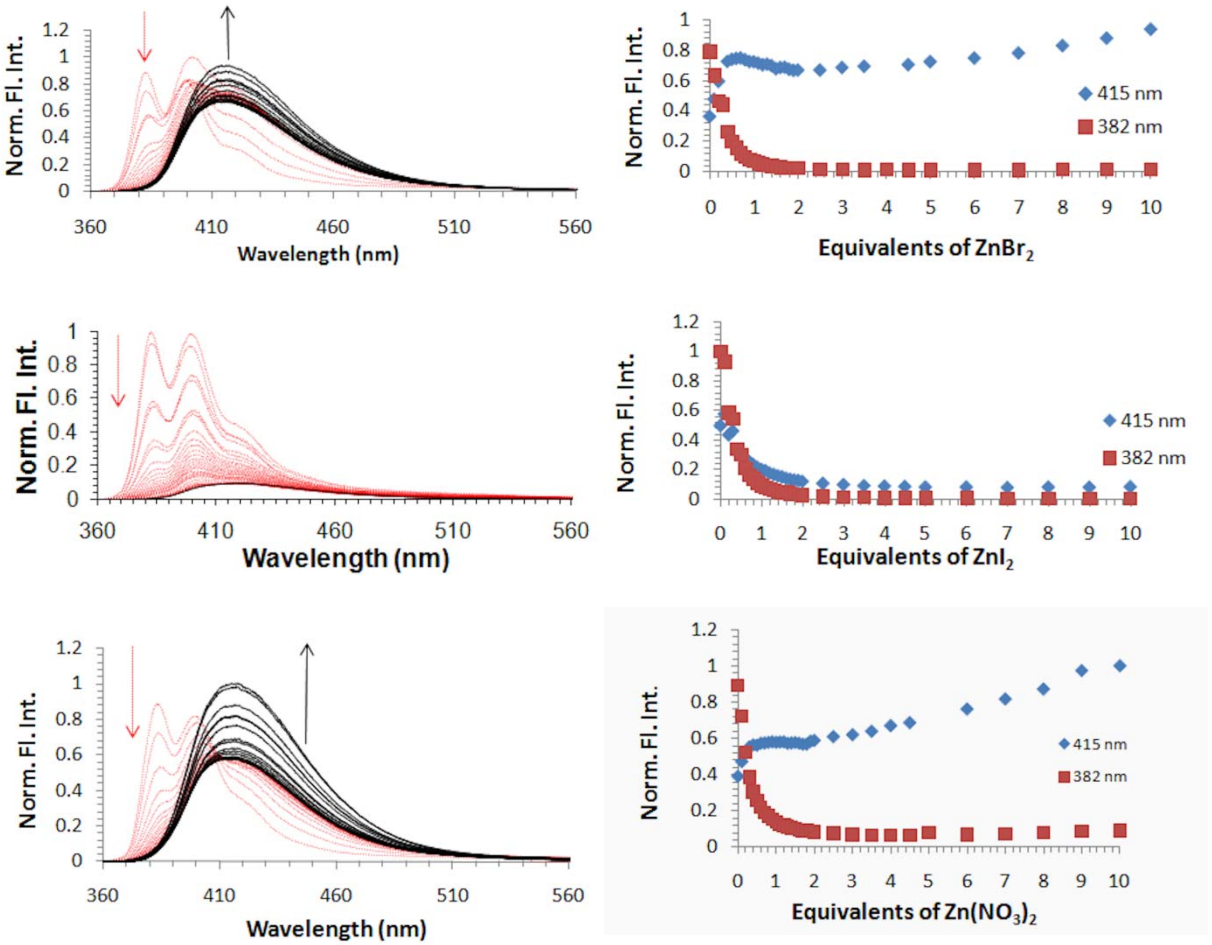
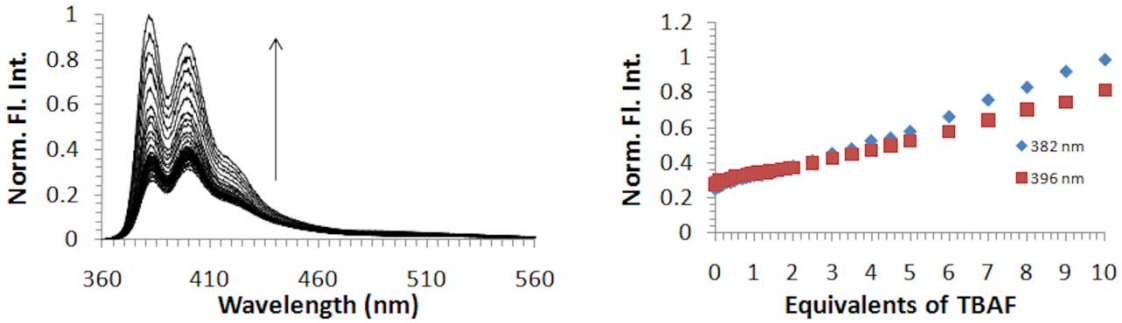


Figure S2: Fluorescence spectra (LHS) and binding isotherm (RHS) between compound **3** and the addition of Zn^{2+} salts.



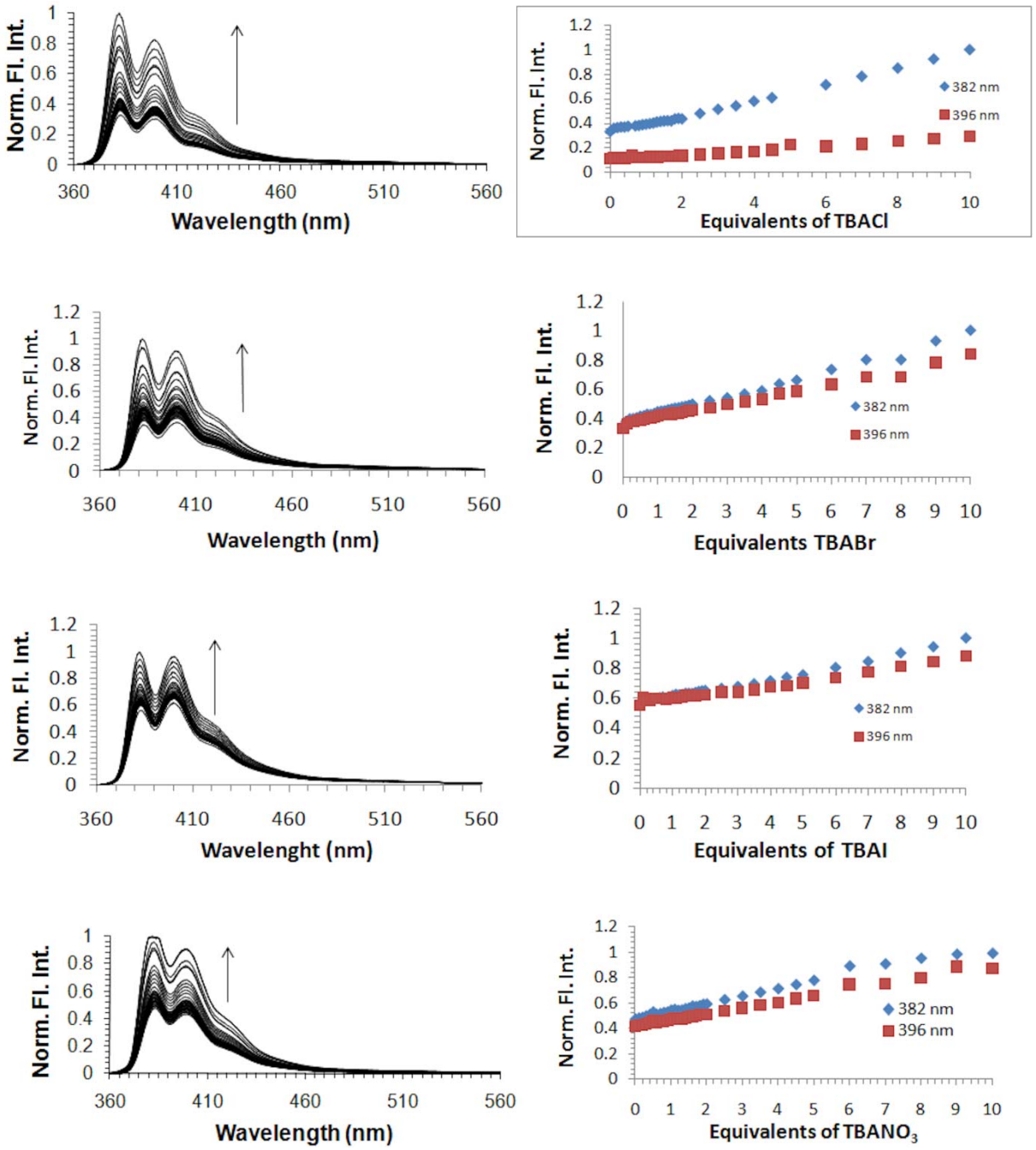


Figure S3: Fluorescence spectra (LHS) and binding isotherm (RHS) between compound **3** and the addition TBA(II)X salts (X = F^-, Cl^-. Br^-. I^- and NO_3^-).

^{1}H NMR titrations: A 10 mM solution of compound **3** was prepared by dissolving 2 mg in 0.5 mL CD_3CN. A 10 times more concentrated solution of the Zn^{2+} salt was prepared in CD_3CN. Aliquots of 5 μL (5 μL = 0.1 equivalent of metal salt) were added to compound **3**, and the ^{1}H NMR spectrum recorded after each addition. The binding constants were determined from ^{1}H NMR spectrum recorded after each addition. The binding studies were pursued by ^{1}H NMR titrations using HypNMR 2008.[4] The signals followed in the NMR experiment are highlighted in Figure S4 and the binding isotherms are shown in Figures S5 to S8 for Br^-, Cl^-, I and NO_3^-, respectively.

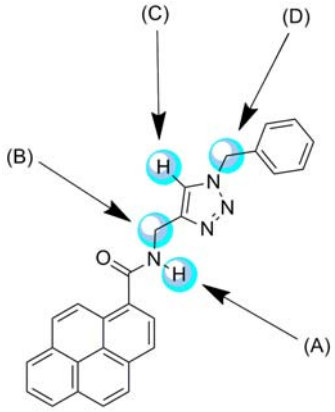


Figure S4: ^{1}H NMR assignments that are followed in the NMR titration experiments.

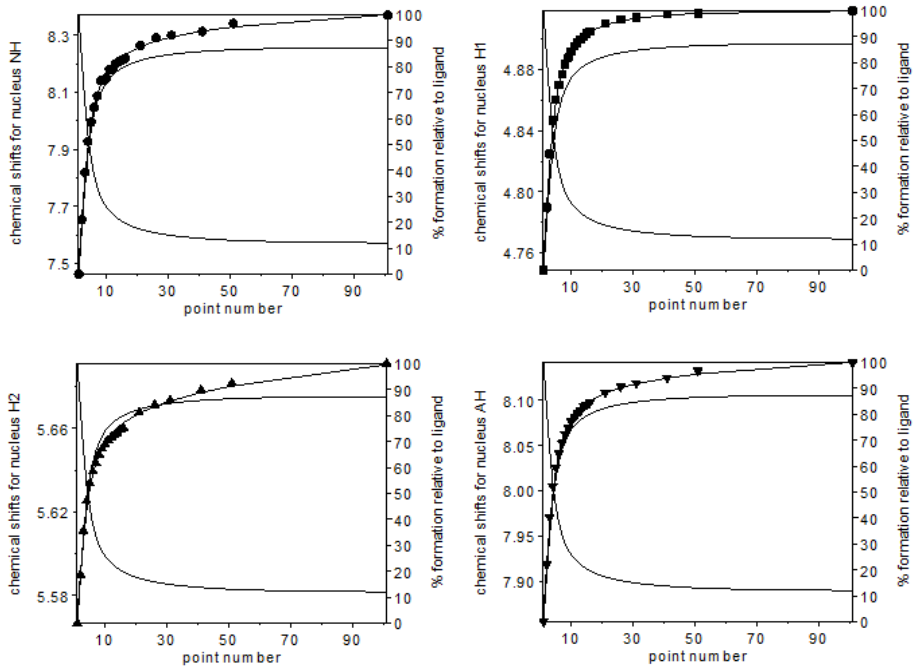


Figure S5: ^{1}H NMR Binding isotherms compound **3** plus the addition $ZnCl_2.xH_2O$.

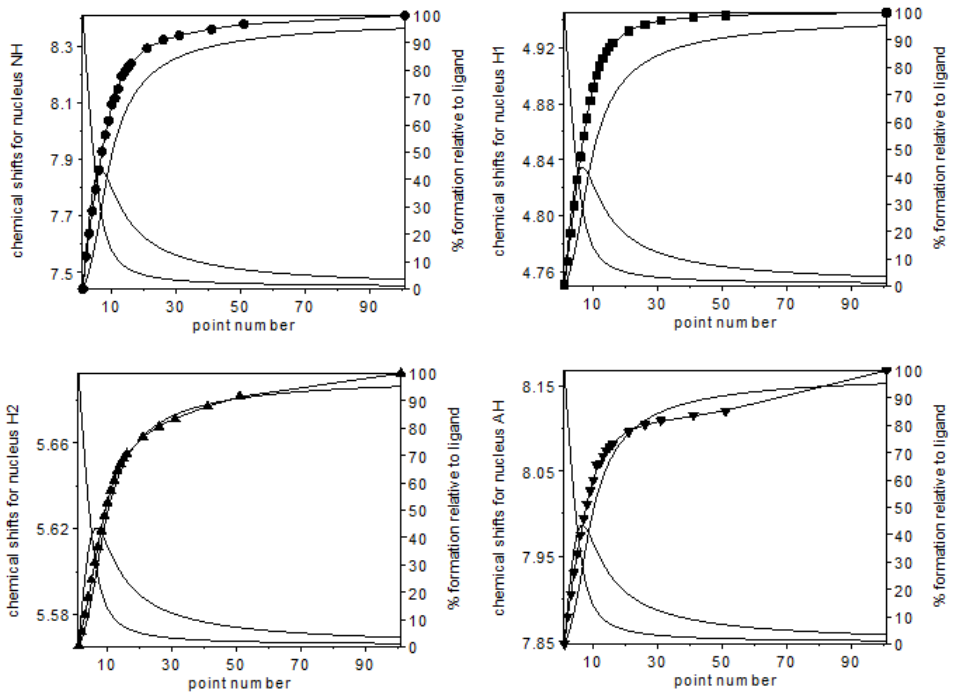


Figure S6: ^{1}H NMR Binding isotherms compound **3** plus the addition $ZnBr_2.xH_2O$.

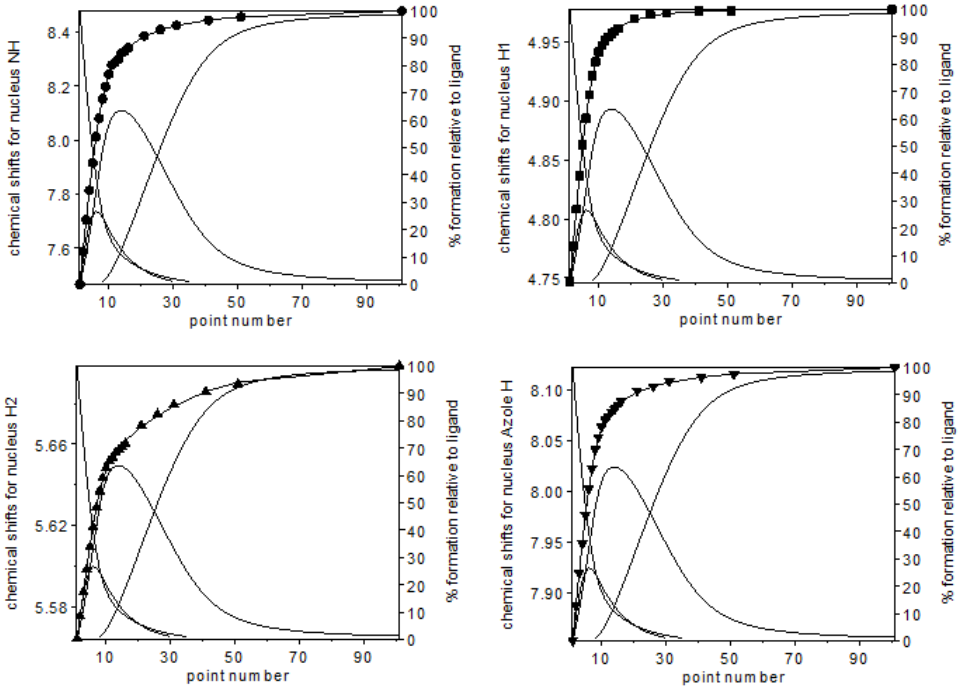


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Figure S7: ^{1}H NMR Binding isotherms compound **3** plus the addition $ZnI_2.xH_2O$.

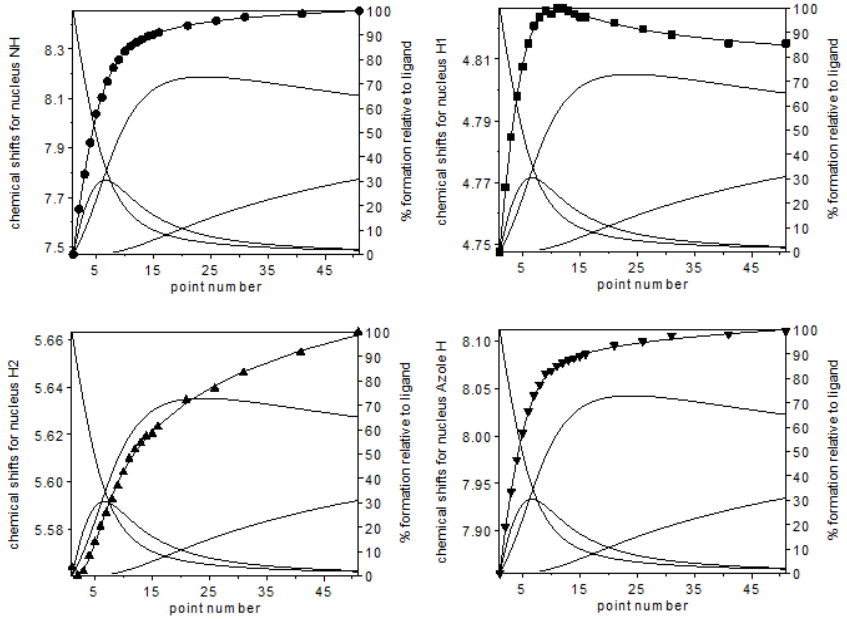
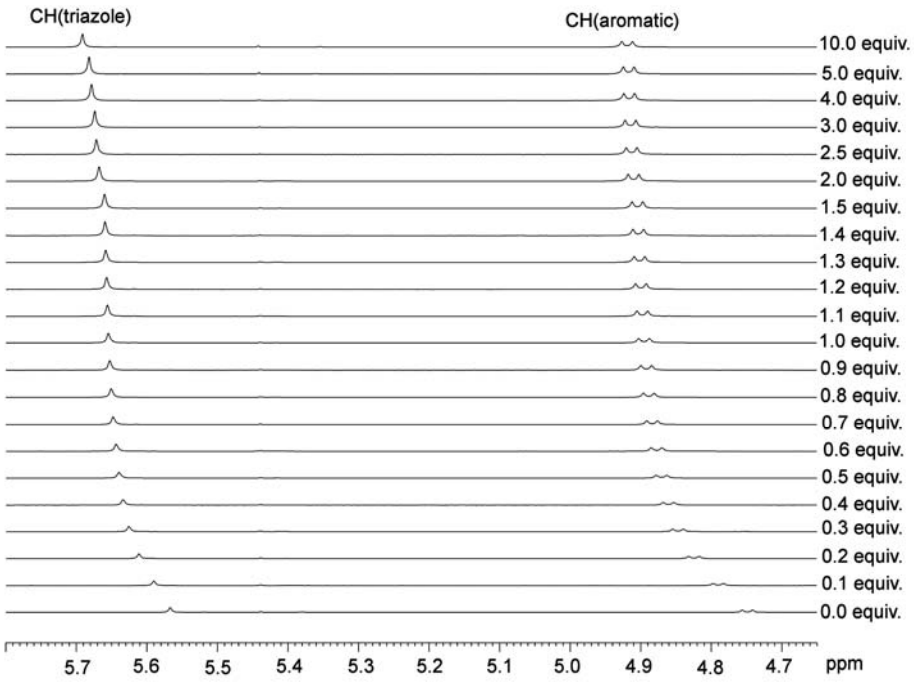


Figure S8: ^{1}H NMR Binding isotherms compound **3** plus the addition $Zn(NO_3)_2.xH_2O$.

(A)



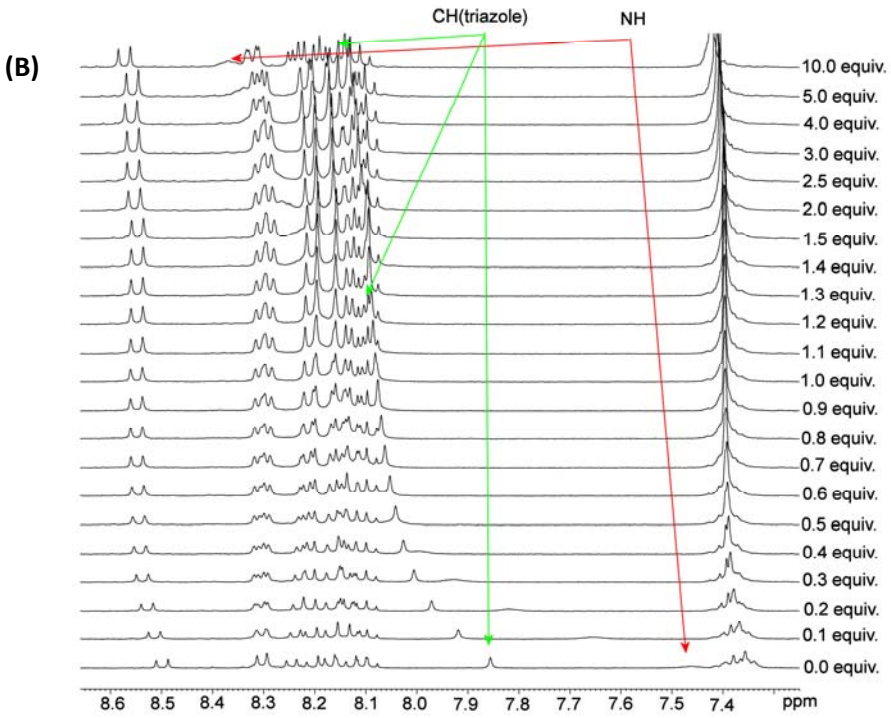


Figure S9: ^{1}H NMR Stack plot: Addition of $ZnCl_2$ with compound **3** in CD_3CN (A) CH_2 and (B) aromatic protons.

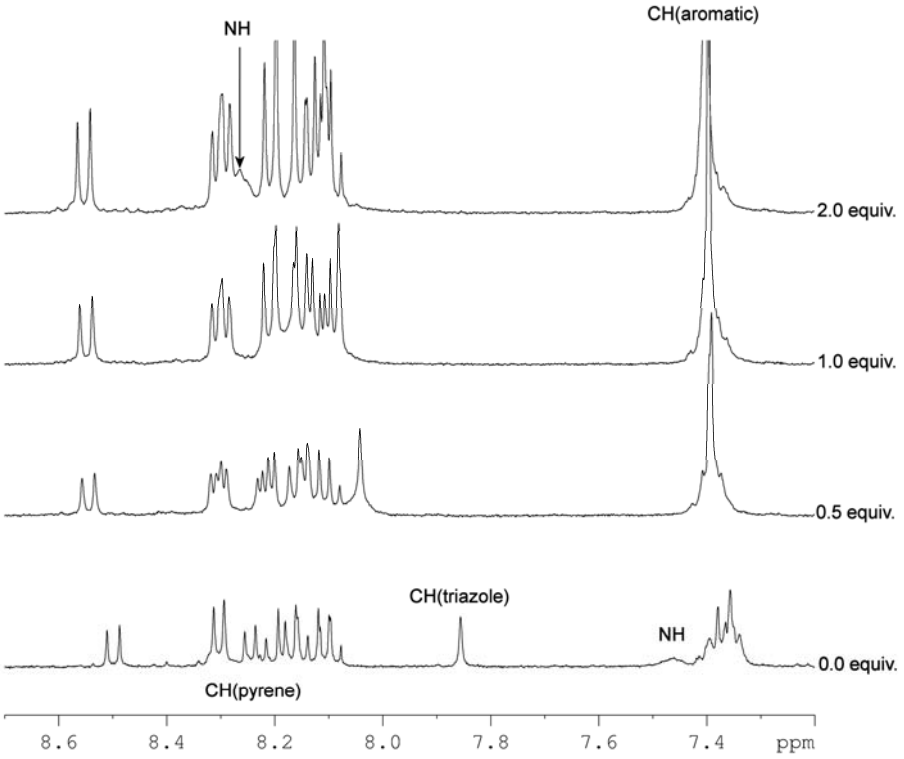


Figure S10: Partial ^{1}H NMR Stack plot: Addition of $ZnCl_2$ with compound **3** in CD_3CN (aromatic region only).

Table S1: Binding constants (K_{21} & K_{11}) determined by ^{1}H NMR and fluorescence titrations for the interactions between compound **3** and Zn^{2+} salts.

	K (M^{-1})	NMR	Fluorescence
$ZnCl_2$	K_{11}	≈ 0	≈ 0
	K_{21}	1.3×10^5	1.8×10^6
$ZnBr_2$	K_{11}	1.7×10^3	1.3×10^4
	K_{21}	5.2×10^5	1.2×10^2
ZnI_2	K_{11}	3.3×10^3	2.5×10^3
	K_{21}	3.6×10^5	7.4×10^5
$Zn(NO_3)_2$	K_{11}	1.5×10^3	6.3×10^3
	K_{21}	1.1×10^5	5.2×10^4

NOTE: The binding constants for TBAX (X = Cl^-, Br^-, I^- and NO_3^-) were also determined, their values were magnitudes smaller than the Zn^{2+} salts.

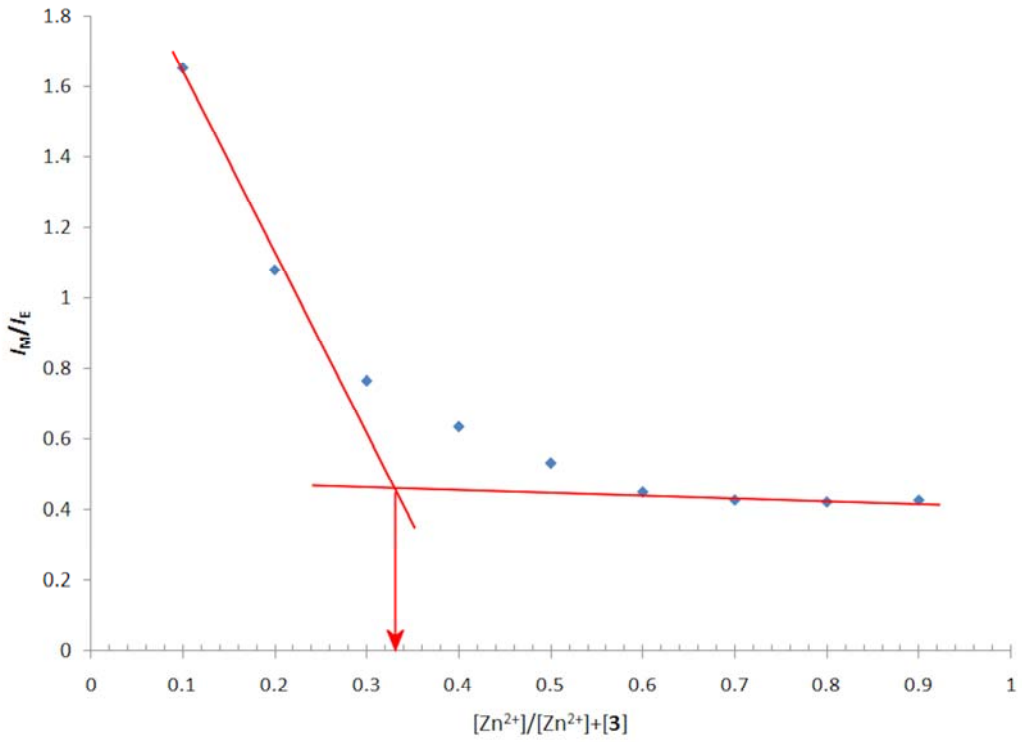


Figure S11: Job's plot of compound **3** with Zn^{2+} obtained by fluorescence measurements. The total concentration of compound **3** and $ZnCl_2$ is 6.48×10^{-4} M where $X \approx 0.33$ (2:1 ligand:metal ratio). The red lines are for visual interpretation only.

Computational methods: All possible isomers for the $L_2Zn(X)_2$ (X = F^-, Cl^- and NO_3^-) complexes were modelled as shown in Figure S13: two tetrahedral enantiomers with non-coordinated anions (**i** and **ii**); two octahedral enantiomers with anions bound in *cis* positions and ligand nitrogen atoms *trans* to each other (**iii** and **iv**); two octahedral enantiomers with anions bound in *cis* positions and ligand nitrogen atom *cis* to each other (**v** and **vi**); one octahedral isomer with anions bound in *trans* positions and ligand nitrogen atoms *trans* to each other (**vii**); one octahedral isomer with anions bound in *trans* positions and ligand nitrogen atoms *cis* to each other (**viii**).

The equilibrium conformers for structures **i** through **viii**, as the dinitrate complexes, were determined using full conformational searching and molecular mechanics energy minimization methods (MMFF) within Spartan '10 installed on a desktop computer equipped with Intel Xenon Dual Quad Core CPUs running at 2.33 GHz. Formal bonds between Zn^{2+} and the ligands and anions were then removed and the geometries reoptimised. The relative energies of the unconstrained complexes are given in figure S13. The unconstrained five structures collapsed into either structure **vii** or **viii**. Structure **viii** has the potential for excimer activity, as observed experimentally, whereas **vii** does not. Structures **vii** and **viii** were used as starting points for equilibrium geometry calculations. Initial refinement was at the semiempirical PM3d level and the resulting structures used as input coordinates for density functional calculations (B3LYP/6-31G*). Calculations were undertaken in the gas phase as the titrations were carried out in mixed solvents for which adequate solvation models have yet to be developed. In the gas phase the binding energy of the *syn*-$\mathbf{3}_2ZnCl_2$ was -230.34 $kJmol^{-1}$; the *anti* conformer was less stable at -184.83 $kJmol^{-1}$. The large values reflect complexation in the gas phase and the experimental binding energies would be expected to be considerably lower due to the competitive nature of the solvents.

Binding energies were determined as:

$$\Delta E_{(binding)} = E_{(complex)} - (E_{(Zn2+)} + 2\,E_{(Cl-)} + 2\,E_{(ligand)})$$

Energies used are those of the geometry optimised complex and free ligand.

A similar protocol was adopted for the L_2ZnF_2 and L_2ZnCl_2 complexes. In both cases the halides remained closely associated with the Zn^{2+} which formed a tetrahedral core to the complex. Zn^{2+} bound two halides and a carbonyl oxygen from each ligand. The angle between the pyrene rings was found to be 76.1° for the fluoride complex and 4.9° for the chloride complex. Data from the density functional calculations are given in Table S2.

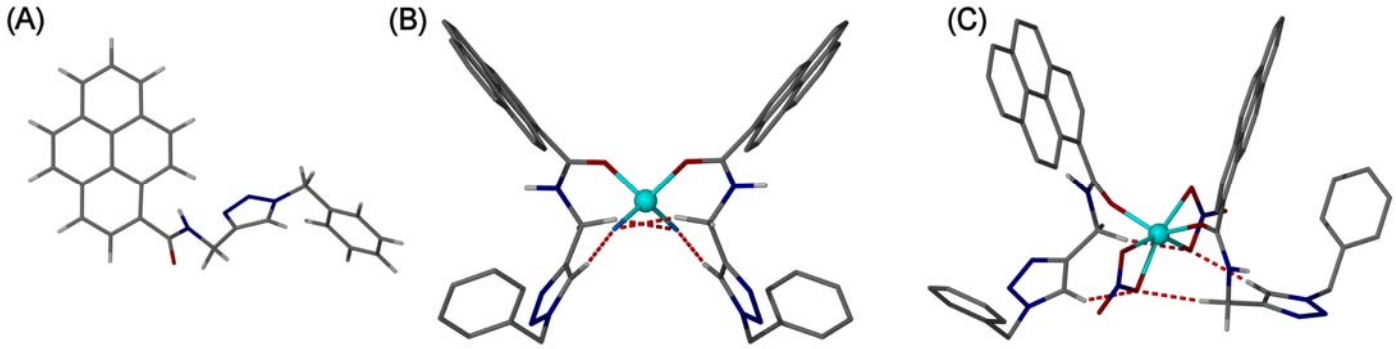


Figure S12: Molecular Models of compound **3** (A) and *syn* $\mathbf{3}_2ZnF_2$ (B) and *syn* $\mathbf{3}_2Zn(NO_3)_2$.

Table S2: X-H and X-H···halide distances in angstroms (Å).

	Free Ligand (A)	L_2ZnF_2 (B)	*syn*-$L_2Zn(NO_3)_2$ (C)*	L_2ZnCl_2 (in paper)
N-H	1.009	1.013	1.011	1.012
TriazoleH	1.079	1.085	1.082	1.081
TriazoleH…anion	N/A	1.930	2.303	2.683
CH_2(amide) …anion	N/A	2.376	2.457	2.783
BzH…anion	N/A	1.930	2.456	3.008
Pyrene excimer angle (°)	N/A	76.06	36.38	4.9

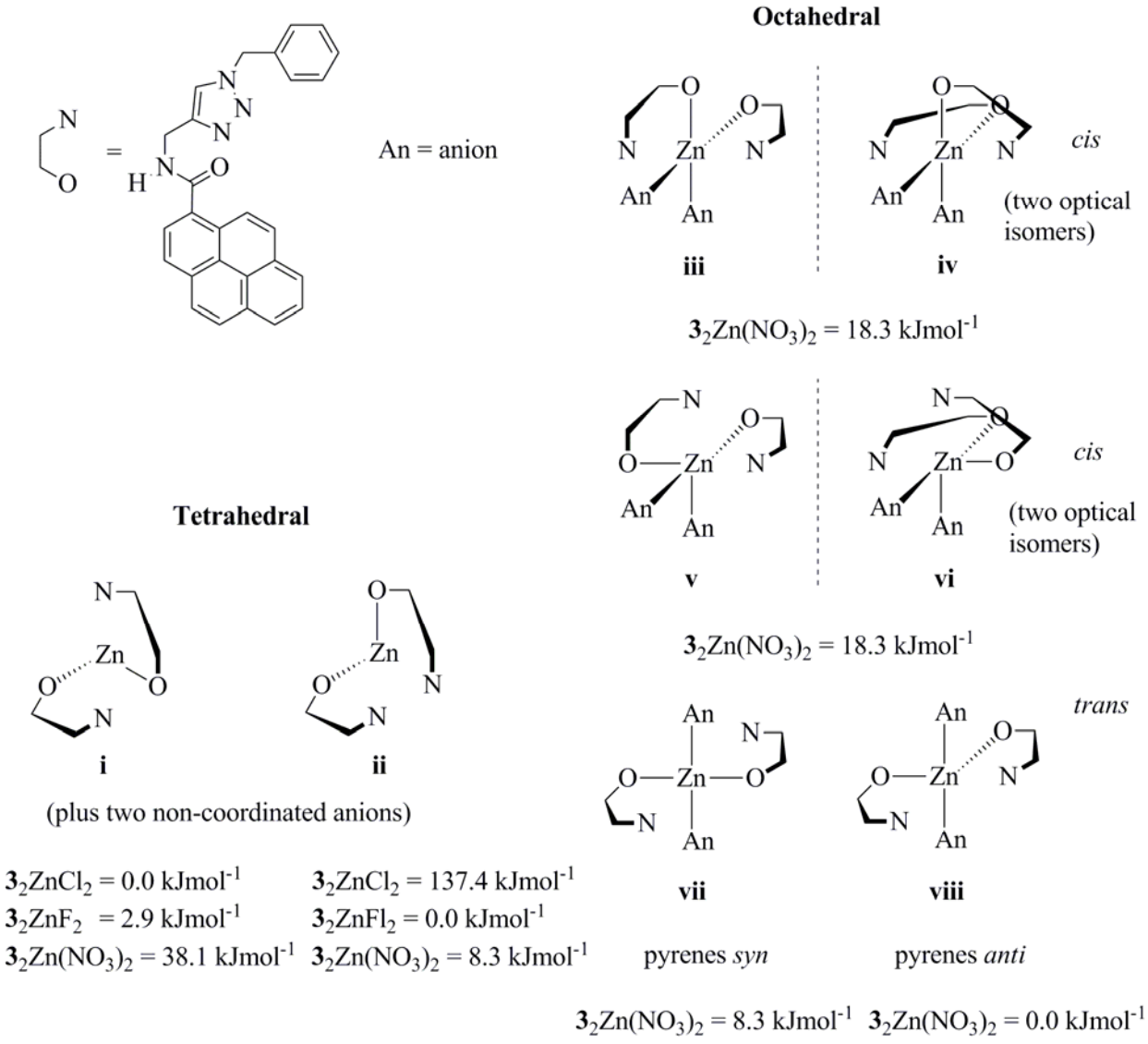


Figure S13. Relative energies of the geometric and optical isomers, for $\mathbf{3}_2ZnX_2$.

2D NMR Spectra:

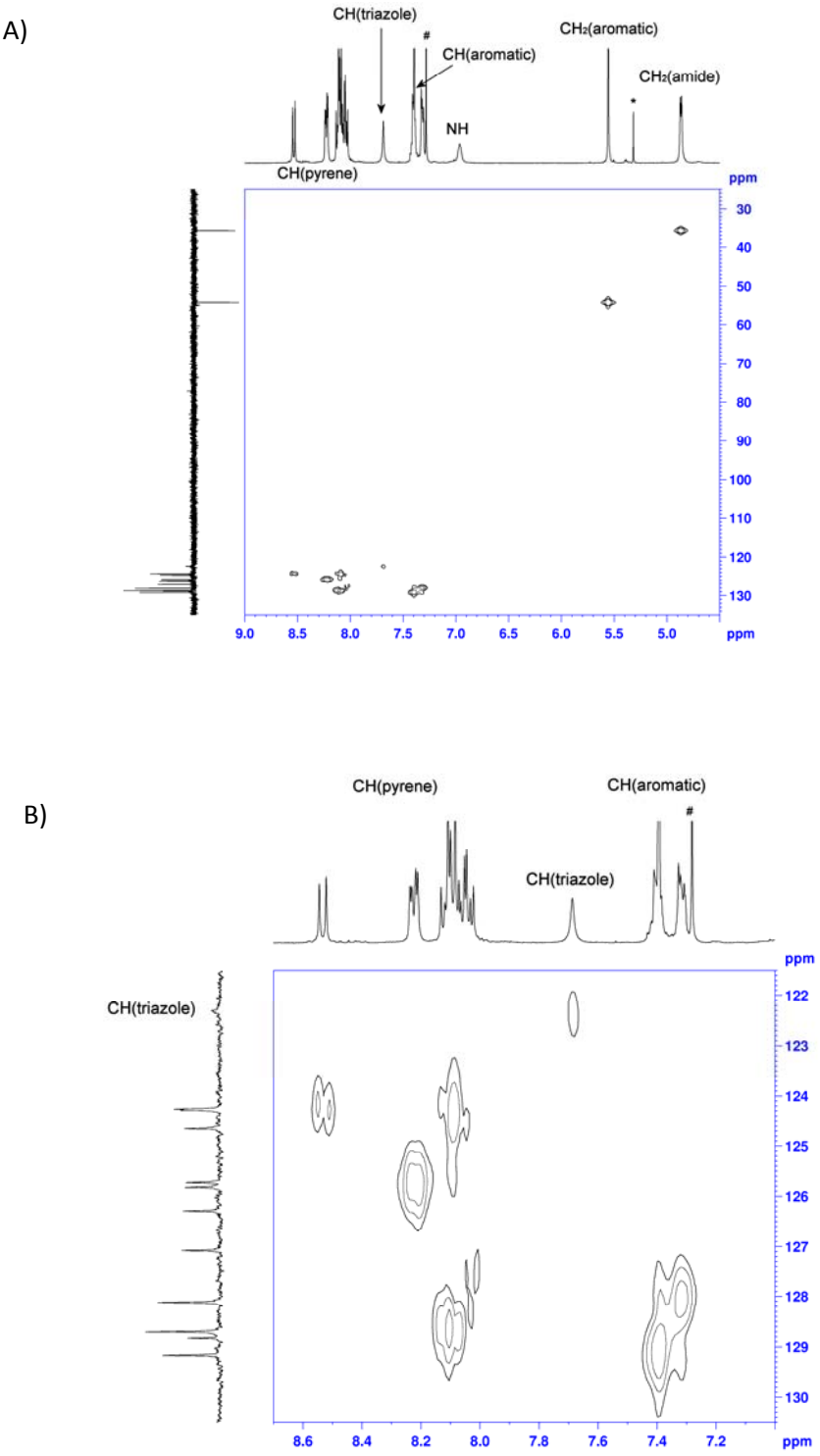


Figure S14: (A) HMQC of compound **3** in $CDCl_3$ (referenced TMS) (B) expanded aromatic region.

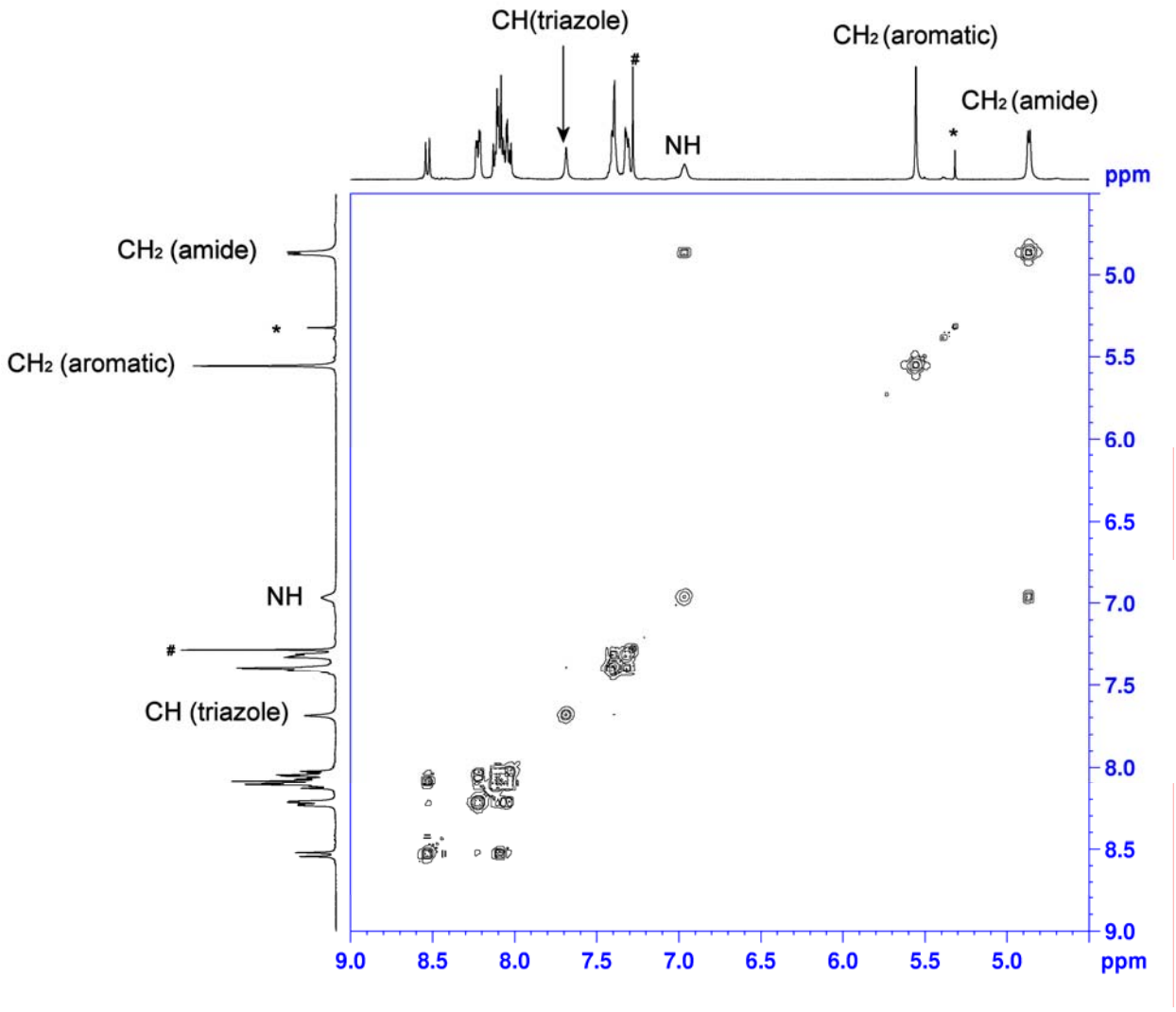


Figure S15: gCOSY of compound **3** in $CHCl_3$ (* CH_2Cl_2 solvent and # $CHCl_3$ solvent)

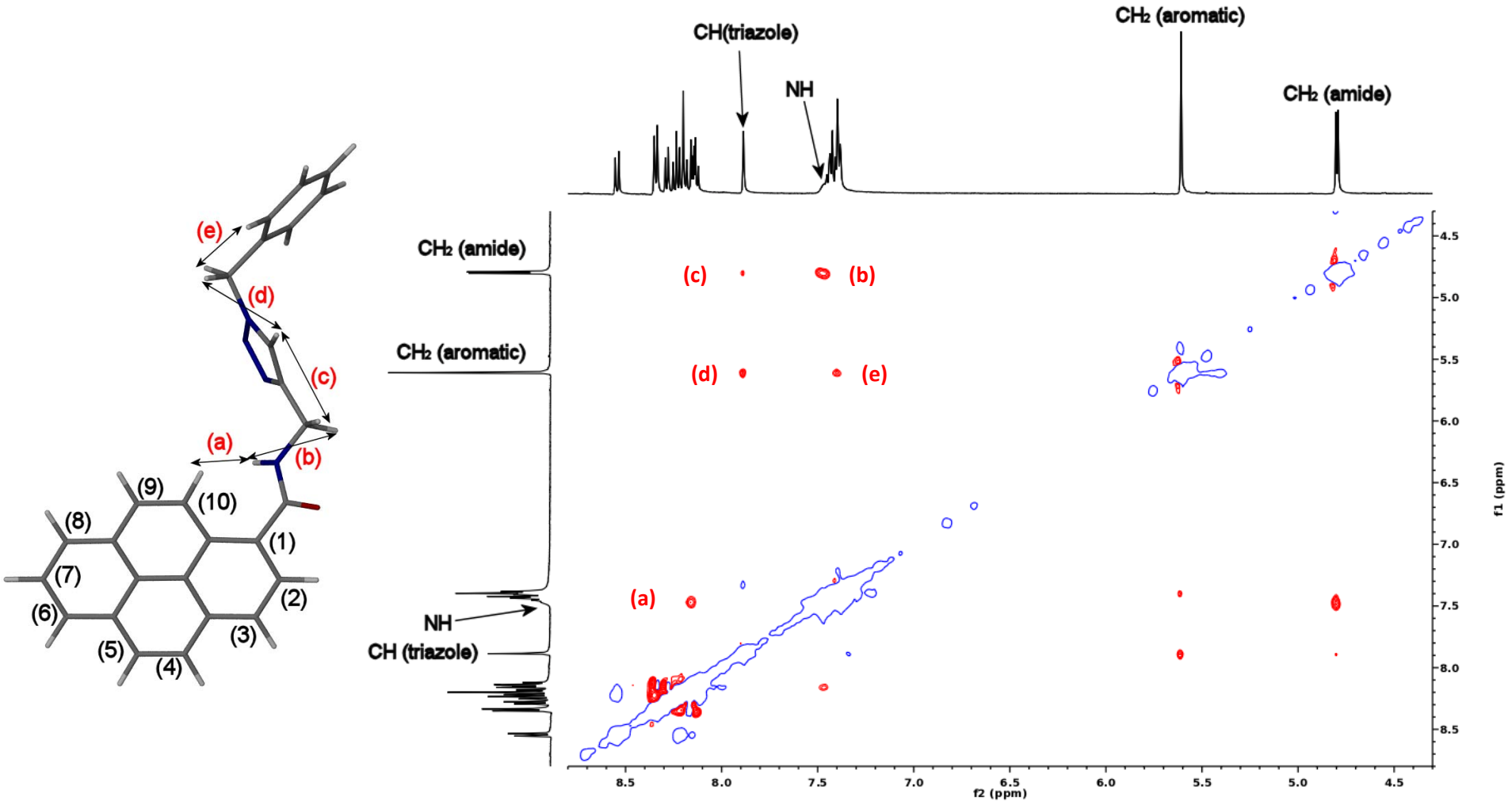


Figure S16: gROSEY compound **3** in CD_3CN. Calculated distances (a) 2.585 Å (b) 2.592 Å (c) 2.861 Å (d) 2.805 Å (e) 2.404 Å.

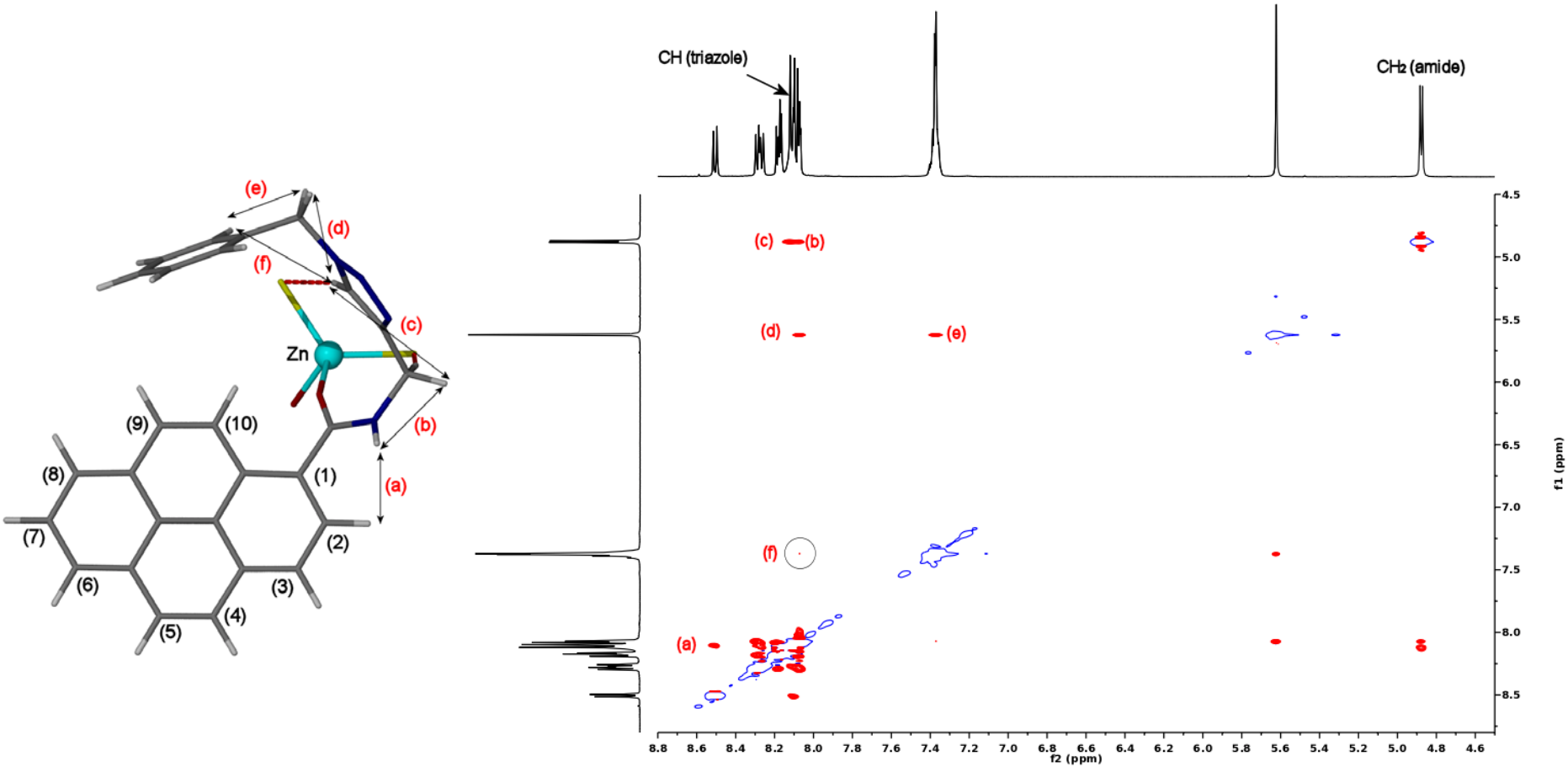
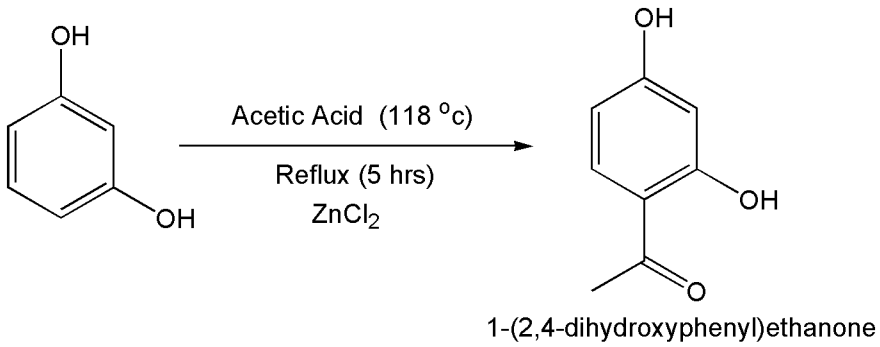


Figure S17: gROSEY compound $\mathbf{3}_2(ZnCl_2)$ in CD_3CN: Note the second ligand has been removed for clarity. Calculated distances (a) 2.386 Å (b) 2.336 Å (c) 2.983 Å (d) 2.738 Å (e) 2.471 Å and (f) 2.961 Å

Friedel-Crafts acylation test: In order to detect any residue $ZnCl_2$ in a reaction, we carried at a straightforward Friedel-Crafts acylation (Scheme S1). The experimental procedure is as follows: To the solution of resorcinol (550 mg, 5 mmol) in 2 mL of acetic acid was added 700 mg (5 mmol) of $ZnCl_2$. The mixture was heated under reflux on the oil bath for 5 h. After cooling, the product was poured into 40 mL of ice water. The precipitate was filtered and recrystallized from water to give desired product as dark red needles (92% yield).[5]



Scheme S1: Preparation of 1-(2, 4 dihydroxphenyl)ethanone via a Friedel-Crafts acylation.

Observations of fluorescence changes, as preliminary tests for Zn^{2+} salts, were made after each test described below:

Test 1. After the reaction, 40 mL of ice water was added to the solution, a red ppt was formed. The solid was collected and the filtrate was tested for residual $ZnCl_2$. This was carried out by preparing a 2 mL solution of compound **3** in CH_3CN (6.48×10^{-4} M). Aliquots of the filtrate were added to the fluorescence cell. Figure S18(A) shows the fluorescence spectrum of compound **3** alone and the addition of filtrate (50 μL). The two spectra are different, however, no clear excimer peak is observed at this concentration. This initial test suggests that we can monitor the residual Zn^{2+}. A more detailed study is under way.

To observe whether or not any metal salt is remaining in the red solid, two additional tests were carried out as described below;

Test 2 (1st crystallization). The red solid which was collected in test 1 above was recrystallized using hot water, upon cooling red needles of the desired 1-(2,4-dihydroxphenyl)ethanone product were collected. The filtrate was then tested for residual $ZnCl_2$ and tested using the same procedure as described above. Figure S18B shows the fluorescence spectrum of compound **3** alone and the addition of filtrate (50

μL). No significant spectral changes were observed, this suggests no Zn^{2+} salt was detected after this process.

Test 3 (pure compound i.e, red needles). The pure compound obtained in test 2 was tested further for residual $ZnCl_2$ by preparing a solution of 1-(2,4-dihydroxphenyl)ethanone (1.31 X 10^{-2} M) in 100% water, small aliquots was again added to a 2 mL solution of **3** as described above no spectral changes are seen. A note of caution; we are not suggesting that all of the $ZnCl_2$ has been removed; using this technique we cannot detect any of the residual salt at this level. Ultimately atomic absorption spectroscopy can be used.

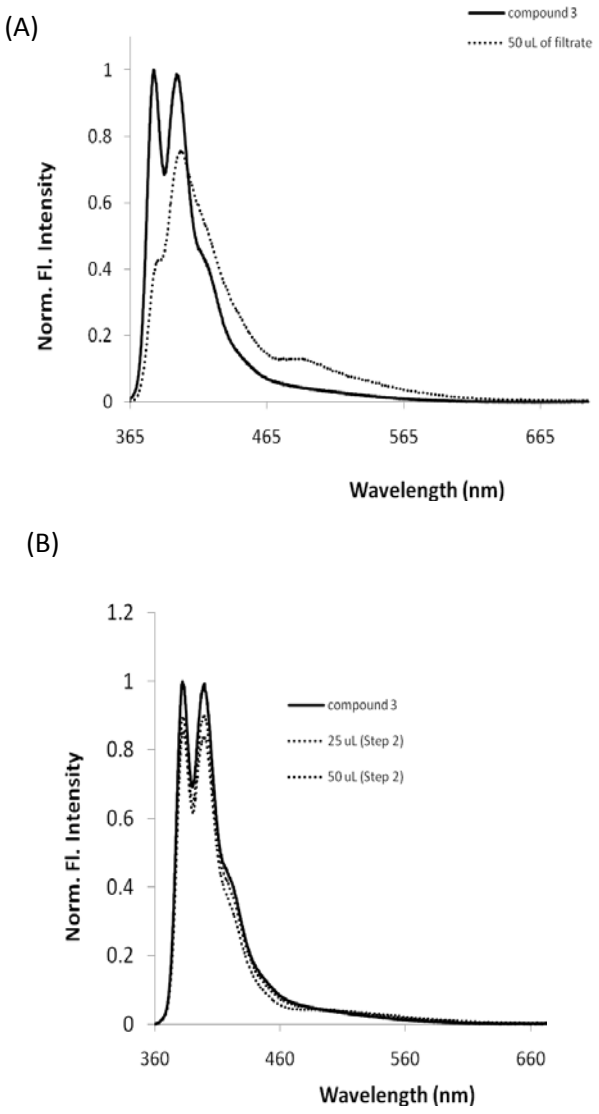


Figure S18: A solution of compound **3** in CH_3CN is prepared (6.48×10^{-4} M). (A) test 1 and (B) test 2.

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