Electronic Supplementary Information

An unprecedented switching of the second-order nonlinear optical response in aggregate bis(salicylaldiminato)zinc(II) Schiff-base complexes

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1. Characterization of the adduct 2

1.1. *^{1}H NMR studies*

The formation of the adduct **2** was investigated by ^{1}H NMR studies. In particular, the addition of an equimolar amount of pyridine to a CD_2Cl_2 solution of **1** involves a down-field shift of H_1, H_3 and the OCH_2- signals, indicative of the deaggregation of the Zn^{II} complex and formation of the adduct **2**.[1] Moreover, the observed up-field shift of the ortho-hydrogen atoms of the pyridine clearly indicates its axial coordination to the complex (Fig. S1).[2]

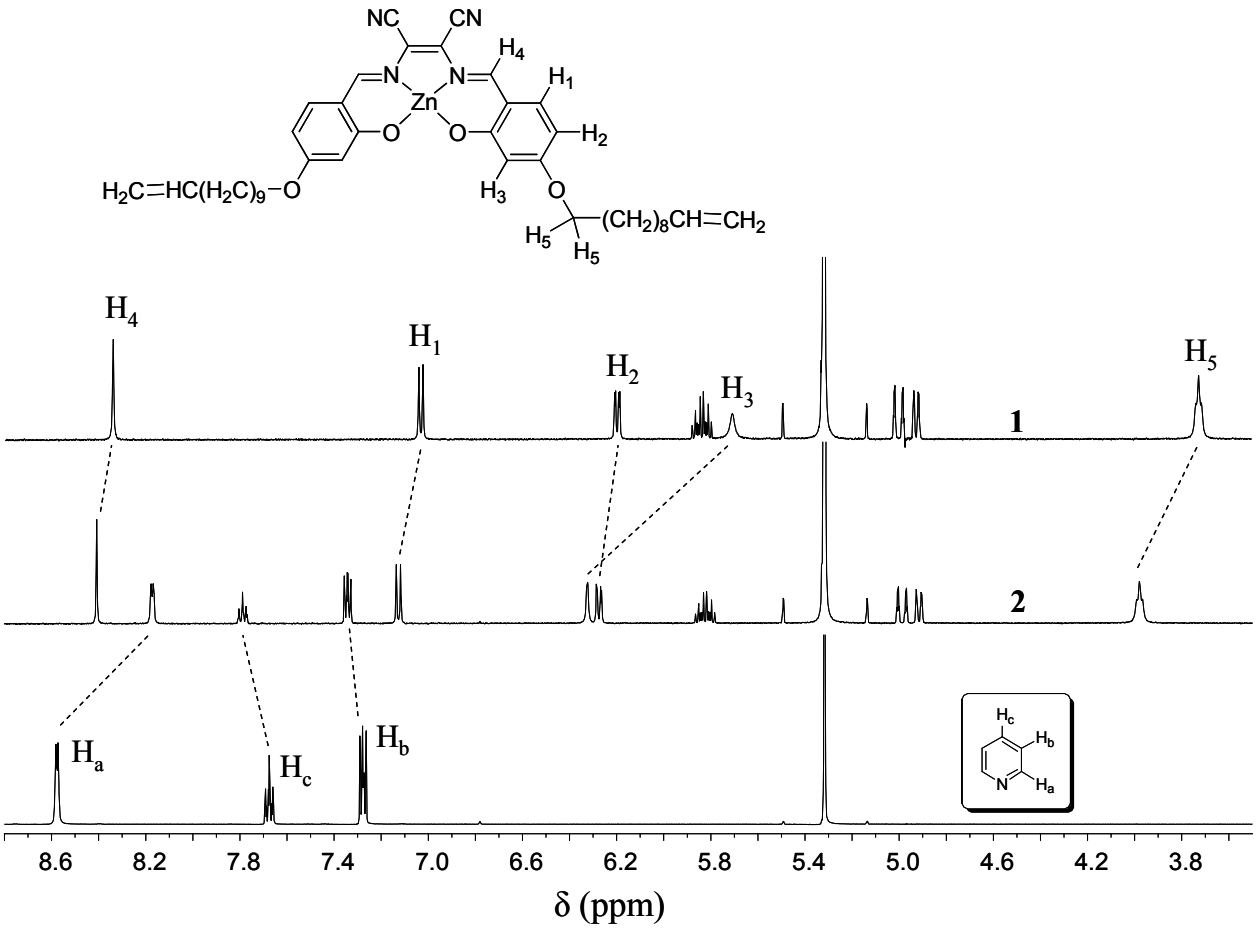

Fig. S1. ^{1}H NMR spectra of **1** (3.0×10^{-4} M) in CD_2Cl_2 and upon addition of an equimolar amount of pyridine, with formation of the adduct **2**. The ^{1}H NMR spectrum of pyridine in CD_2Cl_2 (bottom) is reported as reference.

1.2. *UV/vis spectra*

The addition of 1.2-fold molar amount of pyridine to a DCM solution of **1** involves the deaggregation of the complex and formation of a new band at 555 nm (Fig. S2). Under these conditions this represents the saturation point (no changes of the absorption spectrum are observed by further addition of pyridine) and is indicative of the formation of the adduct **2**.[1]

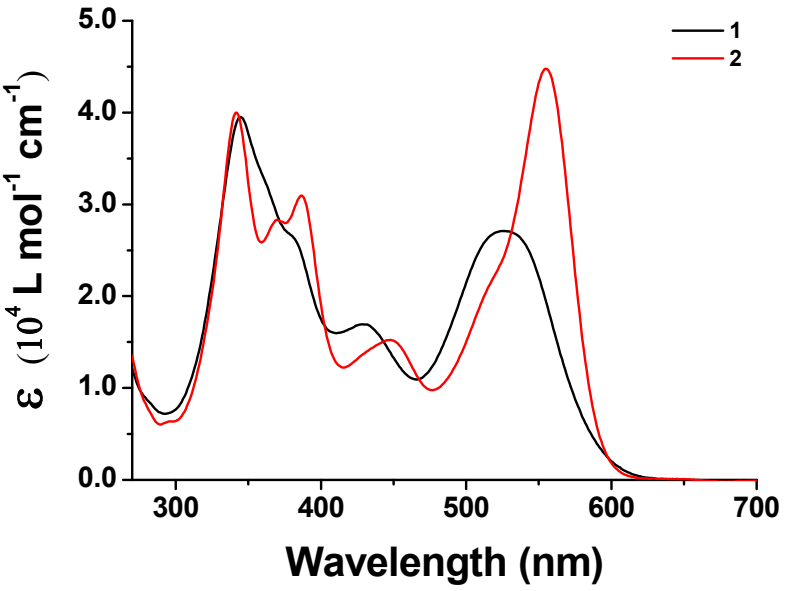

Fig. S2. UV/vis absorption spectra of **1** (3.0×10^{-4} M) in DCM solution, before (—) and after (—) the addition of 1.2-fold molar amount of pyridine.

1.3. *Job's plot analysis*

To determine the binding stoichiometry between the complex **1** and the pyridine, the continuous variation method[3] with absorption data was used. Job's plot analysis (Fig. S3) clearly indicates the formation of a 1:1 adduct.

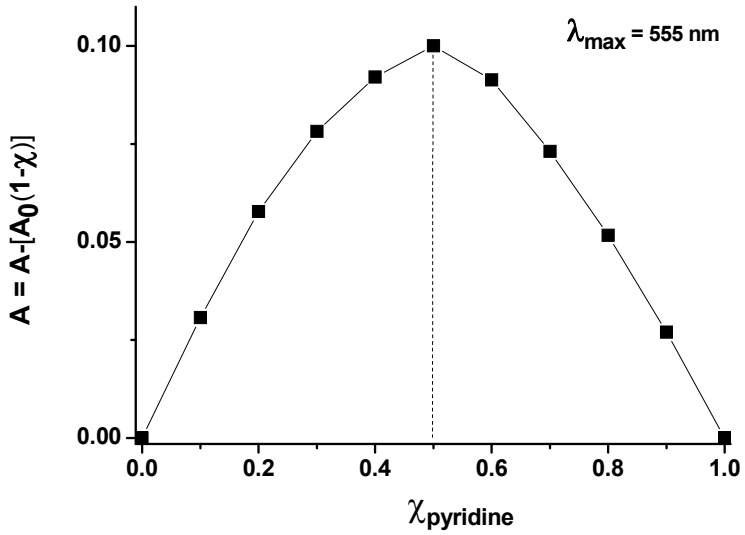

Fig. S3. Job's plot for the binding of **1** with pyridine in DCM. The total concentration of **1** and pyridine is 10 μM. A and A_0 (the initial absorbance of **1**) are the absorbances at 555 nm.

2. Characterization of the adduct 3

2.1. *^{1}H NMR studies*

The formation of the adduct **3** was investigated by ^{1}H NMR studies. In particular, the addition of half molar amount of dpe to a CD_2Cl_2 solution of **1** involves a down-field shift of H_1, H_3 and the OCH_2- signals, indicative of the deaggregation of the Zn^{II} complex and formation of the adduct **3**.[1b] Moreover, the observed up-field shift of the ortho-hydrogen atoms of the dpe clearly indicates its axial coordination to the complex (Fig. S4).

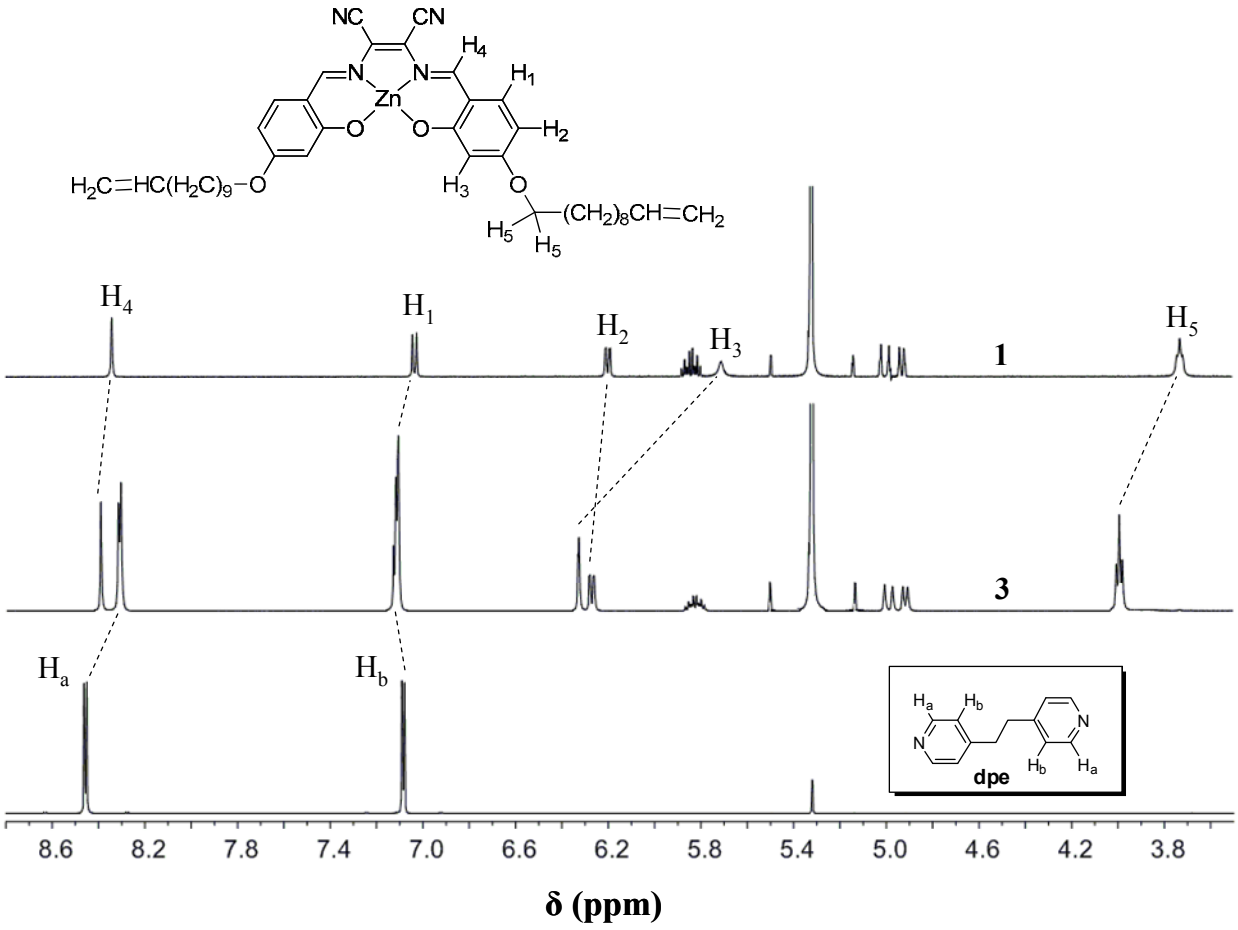

Fig. S4. ^{1}H NMR spectra of **1** (3.0×10^{-4} M) in CD_2Cl_2 and upon addition of half molar amount of dpe, with formation of the adduct **3**. The ^{1}H NMR spectrum of dpe in CD_2Cl_2 (bottom) is reported as reference.

2.2. *UV/vis spectra*

The addition of 0.6-fold molar amount of dpe to a DCM solution of **1** involves the deaggregation of the complex and formation of a new band at 554 nm (Fig. S5). Under these conditions this represents the saturation point (no changes of the absorption spectrum are observed by further addition of dpe) and is indicative of the formation of the adduct **3**.[1b]

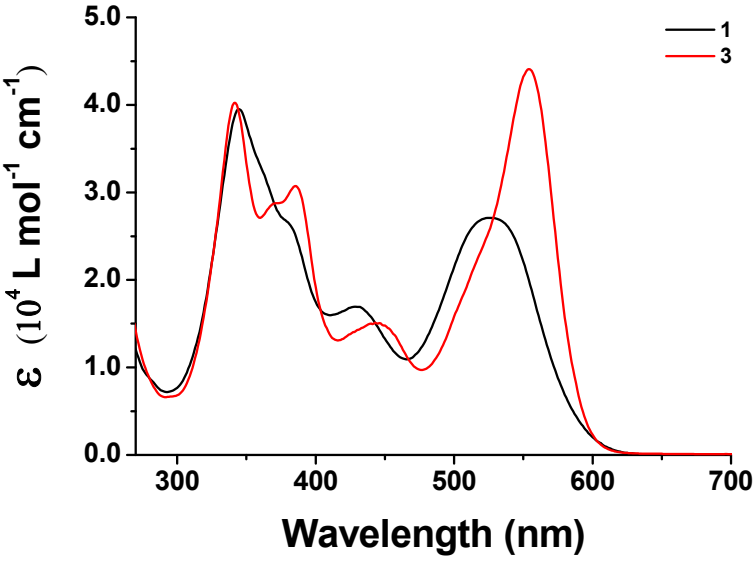

Fig. S5. UV/vis absorption spectra of **1** (3.0×10^{-4} M) in DCM solution, before (—) and after (—) the addition of 0.6-fold molar amount of dpe.

2.3. *Job's plot analysis*

To determine the binding stoichiometry between the complex **1** and the dpe, the continuous variation method[3] with absorption data was used. Job's plot analysis (Fig. S6) clearly indicates the formation of a 2:1 adduct.

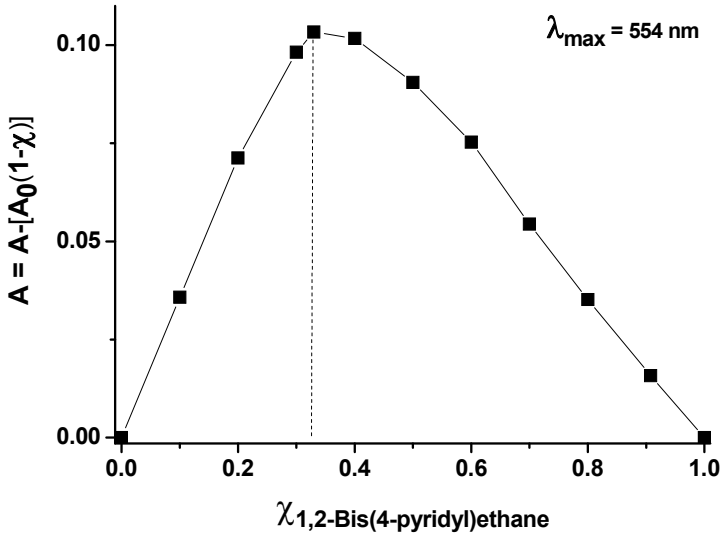

Fig. S6. Job's plot for the binding of **1** with dpe in DCM. The total concentration of **1** and dpe is 10 μM. A and A_0 (the initial absorbance of **1**) are the absorbances at 554 nm.

3. References

1 *(a)* G. Consiglio, S. Failla, I. P. Oliveri, R. Purrello and S. Di Bella, *Dalton Trans.*, 2009, 10426; *(b)* G. Consiglio, S. Failla, P. Finocchiaro, I. P. Oliveri, R. Purrello and S. Di Bella, *Inorg. Chem.*, 2010, **49**, 5134.

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