Electronic Supplementary Information for Dalton Transactions

Electronic Supplementary Information

Controlling the molecular aggregation. An amphiphilic Schiff-base zinc(II) complex as supramolecular fluorescent probe

Giuseppe Consiglio,[a] Salvatore Failla,[a] Ivan Pietro Oliveri,[b] Roberto Purrello[b] and Santo Di Bella*[b]

[a] *Dipartimento di Metodologie Fisiche e Chimiche per l'Ingegneria, Università di Catania, I-95125 Catania, Italy.*

[b] *Dipartimento di Scienze Chimiche, Università di Catania, I-95125 Catania, Italy. Fax: +39 095 580138; Tel: +39 095 738 5068; E-mail: sdibella@unict.it*

Contents

I. Materials and general procedures……. S2

II. Syntheses …… S2

III. Physical measurements……. S3

IV. Job's plot analysis ……..…..…… S4

V. ^{1}H NMR experiments of **1** in CD_2Cl_2 solutions with pyridine ..……. S5

VI. Calculation of the binding constant……... S6

VII. The deaggregation of **1** in DCM solutions..……..…… S7

VIII. References ..……..... S8

I. Materials and general procedures

Zinc acetate dihydrate, 2,4-dihydroxybenzaldehyde, and 11-bromo-1-undecene (Aldrich) were used without purification. Diaminomaleonitrile (Aldrich) was purified by recrystallization from an ethanol solution. CD_2Cl_2 (Aldrich) was dried over anhydrous potassium carbonate overnight before using. Dichloromethane (Aldrich) *stabilized with amylene* was used to prepare solutions of **1**. Fresh prepared DCM solutions of **1**, obtained from stock solutions 1.0×10^{-3} M, were used for spectrophotometric and fluorimetric measurements.

II. Syntheses

2-hydroxy-4-(undec-10-enyloxy)benzaldehyde. To a solution of 2,4-dihydroxybenzaldehyde (0.690 g, 5.00 mmol) in acetone (20 mL), were added potassium carbonate (0.691 g, 5.00 mmol), 18-crown-6 (0.0661 g, 0.250 mmol), and 11-bromo-1-undecene (1.09 mL, 5.00 mmol). The resulting mixture was heated at reflux with stirring for 48 h, under nitrogen atmosphere. After evaporating the solvent, the brown residue was portioned between 30 mL of ethyl acetate and 20 mL of 1.0 M hydrochloric acid. The organic phase, was washed with brine (2 x 10 mL), dried over anhydrous sodium sulphate and evaporated under vacuum. The oily-brown residue was treated with 15 mL of hot cyclohexane, to give a solution and a residue. The solution was collected by filtration, then the solvent removed by rotavapor. An oily black-violet residue was obtained. The residue was purified by column chromatography (silica gel, eluent: cycloexane/ethyl acetate, 95:5 vol/vol) to afford a pale-yellow oily product (1.45 g, 23%). $C_{18}H_{26}O_3$ (290.40): calcd. C, 74.45; H, 9.02; found C, 75.01; H, 9.12. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ = 1.30-1.48 (m, 12H; C*H*$_2$), 1.80 (m, 2H; C*H*$_2$), 2.03 (q, *J* = 6.5 Hz, 2H; C*H*$_2$-CH), 4.00 (t, *J* = 6.5 Hz, 2H; OC*H*$_2$), 4.93 (dd, *J* = 10.0, 2.0 Hz, 1H; CH=C*H*$_2$), 4.99 (dd, *J* = 17.0, 2.0 Hz, 1H; CH=C*H*$_2$), 5.81 (m, 1H, C*H*=CH$_2$), 6.41 (d, *J* = 2.0 Hz, 1H; Ar*H*), 6.53 (dd, *J* = 2.0, 8.5 Hz, 1H; Ar*H*), 7.41 (d, *J* = 8.5 Hz, 1H; Ar*H*), 9.70 (s, 1H; CHO), 11.48 (s, 1H; OH).

[2,3-bis[[2-hydroxy-4-(undec-10-enyloxy)benzylidene]amino]-2-butenedinitrilato]Zn^{II} (1). To a solution of 2-hydroxy-4-(undec-10-enyloxy)benzaldehyde (0.333 g, 1.15 mmol) in methanol (20

mL), diaminomaleonitrile (0.0620 g, 0.575 mmol) was added under stirring. The mixture was heated at reflux with stirring for 1 h, under nitrogen atmosphere. At the yellow-brown solution, zinc acetate dihydrate (0.126 g, 0.575 mmol), was added and the mixture was heated at reflux with stirring for 1h, under nitrogen atmosphere. After cooling, a red-orange precipitate product was collected by filtration, washed with methanol, and dried (0.308 g, 75%). $C_{40}H_{50}N_4O_4Zn$ (716.24): calcd. C, 67.08; H, 7.04; N, 7.82; found C, 67.50; H, 6.99; N, 7.94. MALDI-TOF: m/z = 715 ($[M+H]^+$, 100%). ^{1}H NMR (500 MHz, THF-d_8, TMS): δ = 1.33-1.50 (m, 24H; CH_2), 1.77 (m, 4H; CH_2), 2.04 (m, 4H; CH_2-CH), 4.00 (t, $^3J_{HH}$ = 6.5 Hz, 4H; OCH_2), 4.95 (m, 4H; CH=CH_2), 5.79 (m, 2H; C*H*=CH_2), 6.20 (dd, $^3J_{HH}$ = 9.0 Hz, $^4J_{HH}$ = 2.5 Hz, 2H; Ar*H*), 6.26 (d, $^4J_{HH}$ = 2.5 Hz, 2H; Ar*H*), 7.17 (d, $^3J_{HH}$ = 9.0 Hz, 2H; Ar*H*), 8.40 (s, 2H; C*H*=N).

III. Physical measurements

Elemental analyses were performed on a Carlo Erba 1106 elemental analyzer. ^{1}H NMR spectra were recorded on a VARIAN INOVA 500 MHz spectrometer, using TMS as internal standard. Optical absorption spectra were recorded at room temperature with a Varian Cary 500 UV-Vis-NIR spectrophotometer. Fluorescence spectra were recorded at room temperature with a Fluorolog-3 (Jobin Yvon Horiba) spectrofluorimeter. The fluorescence quantum yield was obtained using fluorescein (Φ_F = 0.925) in 0.1 M NaOH as standard. The absorbance value of the samples at and above the excitation wavelength was lower than 0.1 for 1 cm pathlength cuvettes. MALDI TOF mass spectra were recorded in linear mode with Voyager-DE PRO (Perseptive Biosystem) mass spectrometer instrument, equipped with a nitrogen laser emitting at 337 nm, with a 3-ns pulse width and working in positive ion mode. The accelerating voltage was 25 KV, the grid voltage and delay time (delayed extraction, time lag) were optimized to achieve a higher mass resolution, expressed as the molar mass of a given ion divided by the full width at half maximum (FWHM). The laser irradiance was maintained slightly above the threshold. [meso-Tetra(pentafluoro phenyl)porphine] 0.1 M in THF solvent was used as matrice. The concentration of the sample was 5 mg/mL in THF solvent. 10 μL of sample solution were mixed with 10 or 30 μL of [meso-Tetra(pentafluoro phenyl)porphine] solution, and 1 μL of each sample/matrix mixture was spotted on the MALDI sample holder and slowly dried to allow matrix crystallization. The better MALDI spectra reported here present a mass resolution 1000-1200 Da.

IV. Job's plot analysis

To determine the binding stoichiometry between the complex **1** and the pyridine coordinating species, the continuous variation method[1] with fluorescence data was used. Job's plot analysis (Fig. S1) clearly indicates the formation of a 1:1 adduct.

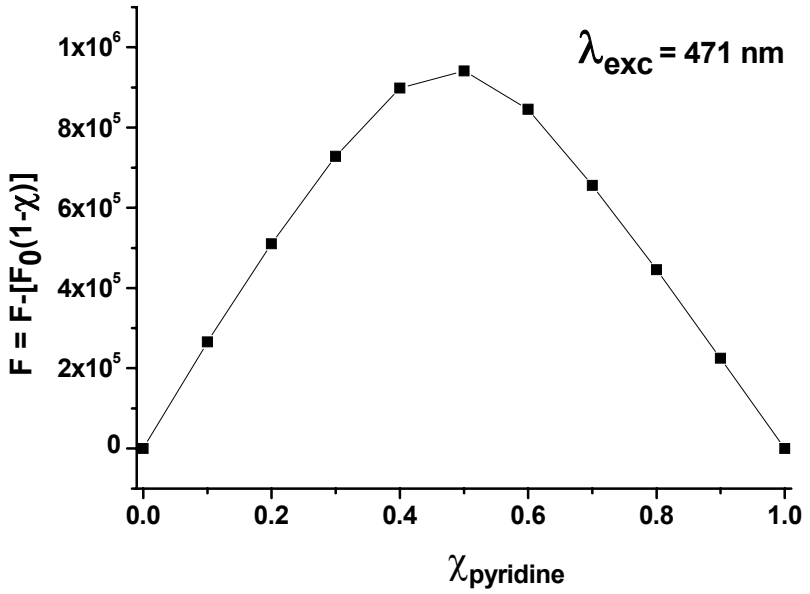

Fig. S1. Job's plot for the binding of **1** with pyridine in DCM. The total concentration of **1** and pyridine is 10 μM. F and F_0 (the initial fluorescence intensity of **1)** are the fluorescence intensities at 598 nm.

V. ^{1}H NMR experiments of 1 in CD_2Cl_2 solution with pyridine

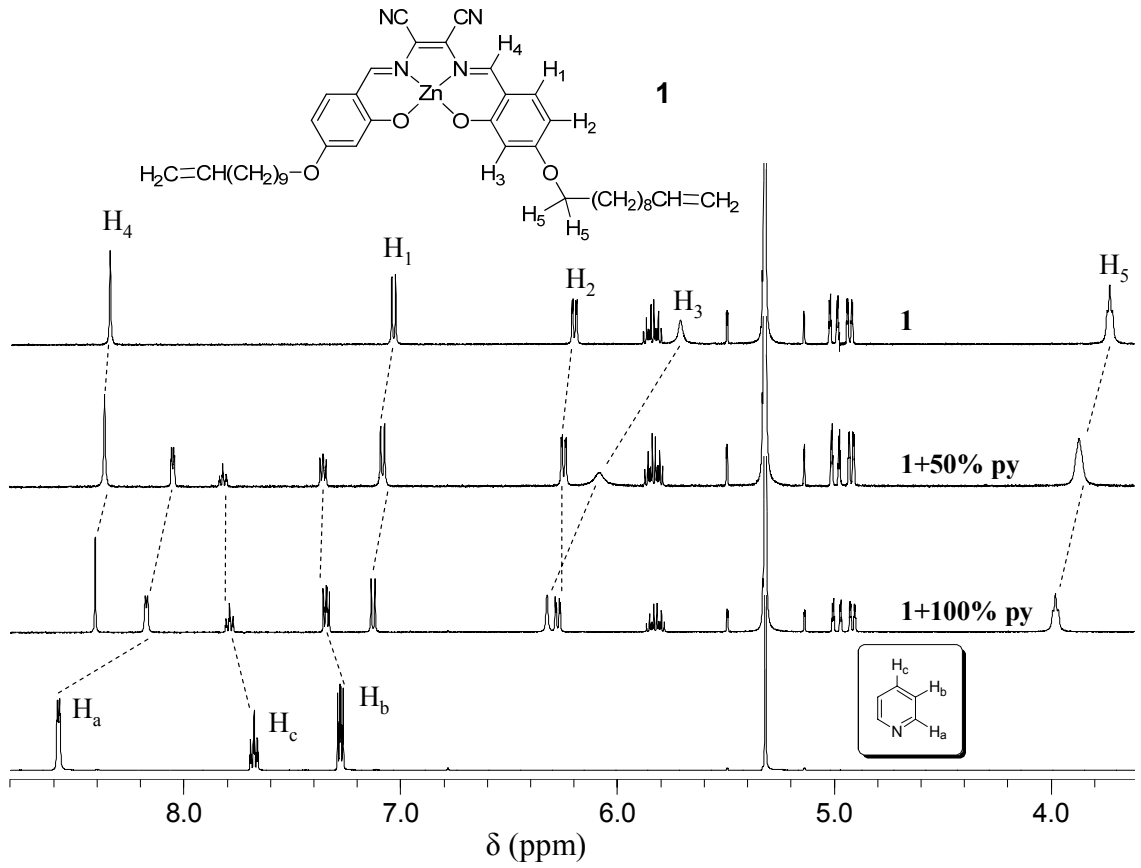

Fig. S2. ^{1}H NMR spectra of **1** (3.0×10^{-4} M; 27 °C) in CD_2Cl_2 and upon addition of 50% and an equimolar (100%) amount of pyridine. The ^{1}H NMR spectrum of pyridine in CD_2Cl_2 (bottom) is reported as reference.

VI. Calculation of the binding constant

The binding constant was calculated from fluorescence titration data by the nonlinear curve fitting analysis of F versus c_p (eq. S1):[2]

$$F = F_0 + \frac{F_{\lim} - F_0}{2c_0}\left[c_0 + c_p + 1/K - \left[\left(c_0 + c_p + 1/K\right)^2 - 4c_0c_p\right]^{1/2}\right] \qquad \text{S1}$$

where F_0 is the initial fluorescence of the solution having a concentration c_0, F is the fluorescence intensity after addition of a given amount of pyridine at a concentration c_p, and F_{lim} is the limiting fluorescence reached in the presence of an excess of pyridine.

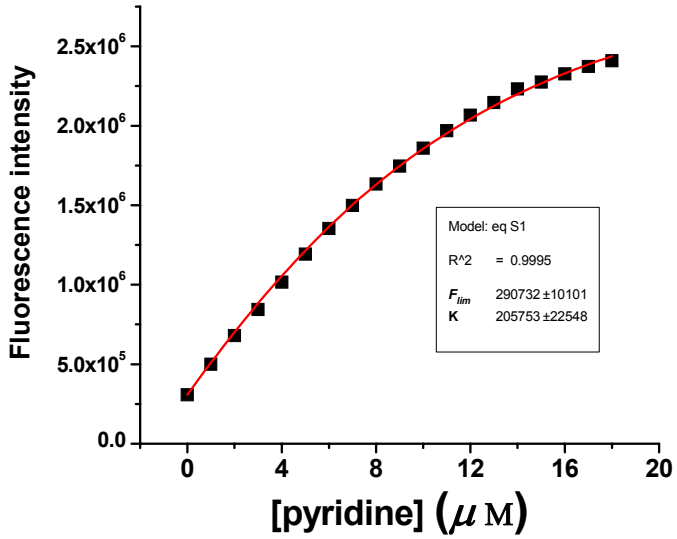

Fig. S3. Variation of fluorescence intensity at 598 nm as a function of the concentration of pyridine added. The solid line represents the curve fitting analysis with equation S1, yielding a log K = 5.3.

VII. The deaggregation of 1 in DCM solutions

The deaggregation of **1** in DCM solutions upon the addition of common coordinating species leads to almost identical optical absorption and fluorescence spectra. However, to obtain the same optical changes as those observed after the addition of an equimolar amount of pyridine, it needs the addition of 100-, 500-, and 10000-fold mole excess of DMSO, THF, and acetonitrile (ACN), respectively (Fig. S4).

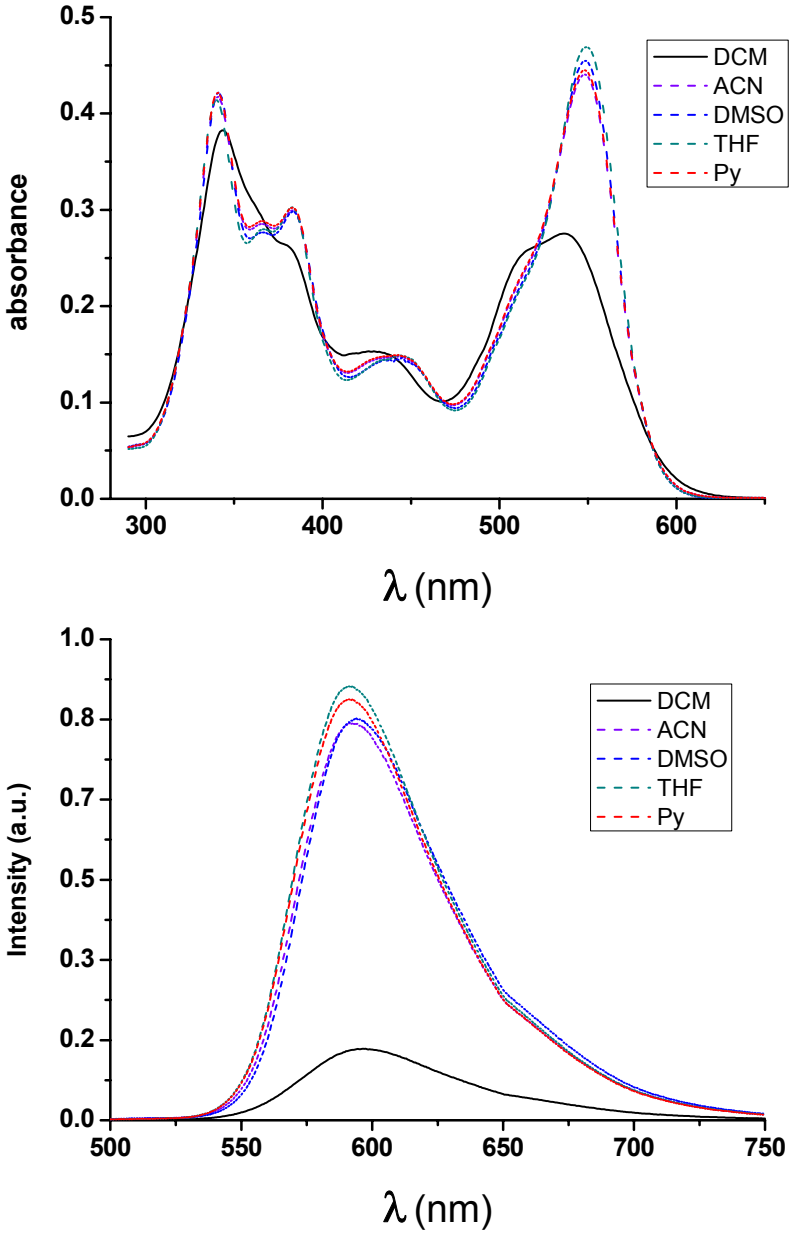

Fig. S4. UV/vis absorption and fluorescence (λ_{exc} = 461 nm) spectra of **1** (1.0×10^{-5} M; 3.0×10^{-8} mol) in DCM solutions, before (—) and after (---) the addition of various coordinating solvents: Py = 3.0×10^{-8} mol; DMSO = 3.0×10^{-6} mol; THF = 1.5×10^{-5} mol; ACN = 3.0×10^{-4} mol.

VIII. References

(1) *(a)* P. Job, *Ann. Chem.,* 1928, **9**, 113; *(b)* V. M. S. Gil and N. C. Olivieira, *J. Chem. Educ.*, 1990, **67**, 473.

(2) J. Bourson, J. Pouget, and B. Valeur, *J. Phys. Chem.*, 1993, **97**, 4552.