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Spectroscopic Properties of Zn(Salphenazine) Complexes and their Application in Small Molecule Organic Solar Cells

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A new family of salphen based complexes, *viz.* Zn(salphenazine)s, has been prepared and is characterized by a larger π -surface compared to previously reported Zn(salphen) complexes. The spectroscopic properties of these Zn(salphenazine)s have been studied in detail using UV-Vis and fluorescence spectroscopy, and further investigated by computational methods. The first application of a Zn(salphenazine) complex in a small molecule organic solar cell (smOSC) is presented showing the potential of salphenazine systems in this area.

Introduction

Organic solar cells (OSCs) have recently attracted considerable attention as low-cost renewable energy sources. OSCs, due to the inherent electrostatic properties of organic semiconductors, rely on the use of a donor/acceptor interface to provide sufficient free energy to separate the photo-generated charges, which are bound together by a strong Coloumbic attraction. Fullerenes have been by far the most utilised and efficient electron acceptors,¹ however a range of donor materials have been shown to produce efficient devices.² Polymeric donor materials, have led the way until recently, with efficiencies as high as 10.6% for a tandem device having been demonstrated.³ However, small molecule donors have made drastic improvements over the past 5-6 years, with devices now close to 9% for a single junction⁴ as well as certified tandem solar cells now at a record 12%.⁵

Small molecules have rapidly evolved as alternatives in this field due to numerous advantages: their straightforward (modular) synthesis and purification, less batch-to-batch variation properties, their intrinsic mono-dispersity and low cost.⁶ In the exploration of novel suitable small molecule donors, various systems have been examined including oligoacenes,⁷ oligothiophenes,⁸ boron dipyrromethenes,⁹ diketopyrrolopyrroles,¹⁰ phthalocyanines,¹¹ merocyanines,¹² squaraines,¹³ porphyrins¹⁴ and mixed porphyrin/phthalocyanine scaffolds (Fig. 1).¹⁵ These latter structures (porphyrins) have shown to possess highly interesting spectroscopic properties due to their unique macrocyclic and conjugated arrangement. Also, considering the fine-tuning of these properties there is a vast amount of literature that shows that a wide range of substituted porphyrins can be accessed with easy variations possible at the *meso* positions of the scaffold. The presence of a metal ion may also be useful to further tune the spectroscopic behaviour, and additionally the Zn(II) family of porphyrins has been frequently used for the creation of supramolecular structures displaying unusual photochemical features.¹⁵

Fig. 1 Some examples of small molecules used in solar cell applications, and schematic structures of a metallo-salphenazine and -salphen.

The application of Schiff base complexes in photovoltaics has been very limited to date,¹⁶ even though Schiff base ligands, and more particularly salen systems, are easily prepared and structurally modified; this intrinsic feature has been demonstrated to be useful in the development and optimization of metal catalysts for highly enantio-selective organic transformations.¹⁷ Nonetheless, in the last few years an increasing interest has been noted in the spectroscopic properties of salphen ligands (Fig. 1)¹⁸ and new interesting applications in field of photo-functional materials have appeared.¹⁷ Che and co-workers reported the application of Pt(salphen) complexes in high-performance OLEDs, and they have shown the importance of the π -conjugation in these salphens.²⁰ In this study, we present the synthesis and a detailed study of the spectroscopic properties of a (relatively) new type of Zn(salphen) complex having a phenazine moiety in the backbone (*i.e.*, a salphenazine complex, Fig. 1).²¹ This alternative

salen scaffold with a more extended π -conjugated structure compared to typical salphen ligands is shown herein to be an attractive candidate for the development of new smOSC.

Results and Discussion

Synthesis

Zn(salphenazine) complexes have been synthesized through a one pot reaction between 2,3-diaminophenazine **A**, substituted salicylaldehydes **B** and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ as templating agent (see Experimental section and Scheme 1). Since 2,3-diaminophenazine **A** is relatively insoluble in a wide range of solvents, the reaction was performed in a minimum amount of DMSO at 100°C. This approach allows maintaining all the reagents and intermediates in solution while the product mostly precipitates after a few hours (in some cases addition of MeOH is needed to obtain the precipitate). Subsequent filtration gave salphenazine complexes **1–7** in fairly good yield (60–73%) and purity; in the case of **1** and **5**, however, the isolated yields were lower (10%) as a result of their higher solubility in MeOH.

Scheme 1 Synthesis of salphenazine complexes **1–7** from precursors **A** and **B**.

With the aim of preparing a Zn complex with a more extensive π -conjugated structure, the synthesis of complex **8** (Scheme 2) has been successfully achieved by applying the synthetic strategy described above using two equivalents of 2-hydroxy-1-naphthaldehyde. Furthermore, by using a previously reported methodology²² an octanuclear, Zn_8 cluster complex **9** characterized by the presence of four salphenazine scaffolds has also been prepared (23% yield) using 2,3-dihydroxy-benzaldehyde, 2,3-diaminophenazine **A** and $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (Scheme 2).

Scheme 2 Synthesis of salphenazine complex **8** and the salphenazine cluster complex **9** from precursor **A** and the required salicylaldehyde derivatives.

Structural analysis

Single crystals suitable for X-ray analysis were obtained by dissolving complex **1** and **5** in hot DMSO (Fig. 2; see also Experimental Section). Similar to previously reported X-ray structures of Zn(salphen) complexes,²³ the Zn ion is slightly tilted from the N_2O_2 binding pocket of the salphen ligand. The axial coordination site in both structures is occupied by a solvent molecule (DMSO) due to the high Lewis acidity of Zn(salphen)s. In order to get more structural information for the structure of complex **9**, its DFT-minimized structure was computed (see the Experimental Section) using previously reported X-ray structures of similar Zn(salphen) clusters as a starting point.²⁰ The computed structure (Fig. 3) shows the assembly of four salphenazine units positioned in a *pseudo* tetrahedral structure with every vertex ending with a phenazine moiety: the latter are thus pointing outward. Four of the in total eight Zn ions are situated in the N_2O_2 pockets (represented in orange in Fig. 3) having an axial H_2O ligand associated. The other four “internal” Zn ions (represented in purple in Fig. 3, see also ESI) are surrounded by five O-atom donors, two of which belong to the same salphenazine unit and the other three form μ_2 -phenoxo bridges between two Zn ions of adjacent salphenazine units.

Spectroscopic properties of Zn(salphenazines)

Typical Zn(salphen)s are generally characterized by two absorption bands in their UV-Vis spectra (200–600 nm region), a first one around 400 nm and a second one around 300 nm (i.e., black trace of compound **10** in Fig. 4). These two bands are influenced by the substituents present in the salphen scaffold; especially the role of the phenyl ring in backbone of the salphen ligand is important. When the latter is substituted with a pyridine ring (designated as “salpyr” complex **11**), for example, an increase in the extinction coefficient ϵ occurs combined with a slight red-shift (see red trace in Fig. 4). Inspired by this characteristic change in the UV-Vis, a further modification of the backbone motif was

realized and a phenazine scaffold was then selected for its presence in many natural dyes.²⁴ As shown in Figure 4, the phenazine contribution to the electronic properties of complex **1** results in a red-shift of 100 nm and a 50% increase of the ϵ of the lower energy band ($\lambda_{\text{max}} = 516$ nm) compared to salphen complex **10** ($\lambda_{\text{max}} \sim 420$ nm). Meanwhile the second absorption band ($\lambda_{\text{max}} \sim 380$ nm) of **1** undergoes in a blue-shift compared to **10** ($\lambda_{\text{max}} \sim 420$ nm, see ESI for more detail).

Fig. 2 Displacement ellipsoid plots at 50% probability level of complex **1** (top) and **5** (bottom). Selected bond lengths (Å) and angles (°) for complex **1**·DMSO: N(1)–Zn(1) = 2.0928 Å, N(2)–Zn(1) = 2.0537 Å, O(1)–Zn(1) = 1.9788 Å, O(2)–Zn(1) = 1.9570 Å, Zn(1)–O(1D) = 2.0862 Å; O(2)–Zn(1)–N(1) = 153.48°, O(1)–Zn(1)–N(1) = 89.13°, O(2)–Zn(1)–O(1D) = 103.47°; Selected data for **5**·DMSO: N(1)–Zn(1) = 2.0717 Å, N(4)–Zn(1) = 2.0765 Å, O(1)–Zn(1) = 1.9554 Å, O(2)–Zn(1) = 1.9807 Å, Zn(1)–O(3) = 2.0658 Å; O(2)–Zn(1)–N(4) = 158.04°, O(2)–Zn(1)–N(4) = 88.22°, O(1)–Zn(1)–O(3) = 102.45°.

Fig. 3 DFT calculated structure for **9**·(H₂O)₄, the orange and the purple spheres represent the Zn ions respectively inside the N₂O₂ and the O₄ coordination pockets. For simplicity, only a partial numbering scheme is shown here. Further snapshots of the structure are presented in the ESI†.

Fig. 4 UV-Vis comparison between Zn(salphen) derivative **10** (black trace), Zn(salpyr) complex **11** (red trace) and Zn(salphenazine) **1** (blue trace) in THF at a concentration of 1×10^{-5} M.

A detailed study toward the spectroscopic properties of Zn(salphenazine) complexes has been carried out using Zn(salphenazine) **1** as model compound due to its higher solubility compared to **2–9**. Furthermore, the presence of four *tert*-butyl groups highly reduces the possibility of formation of dimeric species, which can affect the absorption and emission properties. The UV-Vis spectrum of **1** only slightly changes upon variation of the solvent (Fig. S1, see ESI), and this suggest that the type of electronic transitions that are involved have π - π^* character rather than charge transfer (CT) character. Figure 5 shows the UV-Vis absorption and emission spectra of **1** in THF, which provides the highest ϵ value among all the solvents tested. In the absorption spectra five main bands are observed, two in the visible region (λ

= 384 nm and $\lambda = 516$ nm) and three in the near-UV ($\lambda_{\text{max}} = 231$ nm, $\lambda_{\text{max}} = 257$ nm and $\lambda_{\text{max}} = 328$ nm). Upon excitation of the lowest energy band ($\lambda = 516$ nm), an appreciable emission band at $\lambda = 624$ nm is observed being lower in intensity if the wavelength of excitation is varied to other values.

Fig. 5 Absorption and emission spectra of **1** in dry THF at 1.76×10^{-5} M.

By comparing the UV-Vis spectra of complexes **1-9**, the role of the substituents in the salphenazine ligand has been evaluated (see also ESI Figures S2 and S3). In the case of tetra-substituted **1**, the two bands in the visible region are at slightly lower energy ($\Delta\lambda = 15$ nm) compared to the bands from the di-substituted complex **5** (Fig. S2). The two additional *tert*-butyl groups in the 5- and 5'-positions of the salphenazine scaffold bring about an additional positive inductive effect that would further destabilize the π^* excited state in **1**. Halogens are controversial substituents, since they produce a negative inducting effect and a positive resonance effect. As suggested by TD-DFT calculations (see next section) the resonance effect seems to have a stronger influence on the salphenazine scaffold causing a destabilization of the π^* excited states. This results in a blue-shift of around 31 nm for **2-4** (Fig. S2). Complexes **5-7**, due to the presence of only two substituents (3- and 3'-position in the ligand backbone), are less influenced by the electron-donating and electron-withdrawing groups but show similar effects (see Fig. S3, ESI†).

In order to obtain systems with increased absorbance towards the near IR, two modified synthetic strategies were applied (see Scheme 2). The preparation of a Zn(salphenazine) complex with a more extended π -conjugated system compared to salphenazine complex **1** (i.e., Zn(salphenazine) **8**) was carried out; instead of having two substituted phenyl rings (derived from the salicylaldehyde precursor), complex **8** is characterized by the presence of two naphthyl groups.

The enhancement of the π -conjugation, however, results only in a small improvement of the absorption properties (Fig. 6); a slight red-shift of 8 nm was observed while maintaining a similar value of ϵ compared to complex **1**. This suggests that simple extension of the π -conjugation (i.e., the change from phenyl to naphthyl side groups) does not substantially improve the spectroscopic properties required for an effective application thereof in OSC. Thus, in order to obtain good smOSC candidates the attention was then focused on multinuclear Zn(salen)s with heteroaryl bridging

groups such as present in Zn(salphenazines) as heterocyclic synthons have shown interesting results in heterojunction solar cells.²⁵

Fig. 6 UV-Vis comparison between Zn(salphenazine) complexes **1**, **8** and **9** in THF at a concentration of 1×10^{-5} M.

A second synthetic strategy was considered in order to interconnect multiple chromophores; this was successfully achieved in the preparation of the octanuclear Zn-cluster complex **9** incorporating four Zn(salphenazine) units. As shown in Figure 7, the absorption spectra of **9**, in comparison with **1**, is characterized by a 70% increase in the ϵ value for the band in the visible range. However, the absorption maximum located at 413 nm (100 nm towards the blue with respect to complex **1**) does not make complex **9** suitable for OSC applications.

As previously mentioned, porphyrins and their metal complexes have demonstrated to be good candidates in the preparation of devices for DSC and OSC. Therefore, a comparison between the newly developed Zn(salphenazine) systems and a Zn(porphyrin) would be useful. In Figure 7 the comparison between Zn(salphenazine) complex **1** and Zn(porphyrin) complex **12** is reported. Zn(porphyrin) **12** shows a typical Soret band (at $\lambda = 424$ nm) with a ϵ value of an order of magnitude higher than **1**. On the contrary, complex **1** has an absorption spectrum that covers a wider range of accessible wavelengths. These spectroscopic properties combined with the easy synthesis/functionalization demonstrate that the salphenazine scaffold could be a potential alternative to porphyrins and its derivatives.

Fig. 7 UV-Vis comparison between salphenazine complex **1** and Zn(porphyrin) **12** in THF at a concentration of 1×10^{-5} M.

TD-DFT analysis of Zn(salphenazine)s

TD-DFT was employed for calculating 80 singlet excited states starting from the gas-phase optimized geometry of **1** and **3** with a THF molecule coordinated in the axial position. Experimental and theoretical absorption spectra of complex **1** and **3** in THF are reported in Figure 9 together with the electron density difference maps (EDDMs)²⁶ of the major electronic transitions of the lowest energy band. The solvent effect was taken into account with the CPCM method. A very good agreement between the experimental and simulated UV-Vis spectra was observed for **1**; the three bands shown in the experimental spectrum are blue-shifted only by 5 nm in the DFT calculated UV-Vis trace. Despite this excellent agreement, TD-DFT significantly overestimates the extinction coefficient of the two highest energy bands. The lowest energy band is formed by two electronic transitions: the first one at $\lambda = 534$ nm (2.32 eV) with small oscillator strength (0.035) and the second one at $\lambda = 511$ nm (2.43 eV) with oscillator strength of 0.54. Both transitions are shown to have a π - π^* character with no contribution from the metal centre, in particular the electron density migrates from the two phenyl side groups towards the salphenazine backbone as represented in the EDDM of the major transition 2 (Fig. 8A, at the right).

Fig. 8 Calculated (blue and green lines) and experimental (black dotted lines) absorption spectra of **1** (A) and **3** (B) in THF. The excited states are shown as vertical bars and the transition 2 for complex **1** (C) and complex **3** (D) is represented below with electron density difference maps (EDDMs, the electron density migrates from the violet to the blue lobes). Energy values, oscillator strength values and major orbital contributions are reported beside the EDDMs.

The other two bands at higher energy (at $\lambda = 389$ nm and 326 nm, respectively) are also based on π - π^* transitions (see EDDMs of transition 7, 13 and 14 in the ESI†), and this is in line with the observations done in the UV-Vis experiments carried out in

different solvents (see Fig. S1, ESI). In the case of Zn(salphenazine) complex **3** the computed spectrum is in reasonable agreement with the experimental one, and a blue-shift of 15 nm of the lowest energy band is now observed. Through analysis of the type of transition involved in the UV-Vis spectrum of **3**, similar $\pi\text{-}\pi^*$ excited states were found as observed for Zn(salphenazine) complex **1** (EDDM in Fig. 8B). In order to understand the 44 nm blue-shift of the lowest energy band caused by the substitution of the four *tert*-butyl groups in **1** with four Cl atoms present in **3**, frontier molecular orbital (FMO) analysis has been carried out. Figure 9 shows that the Cl substituents significantly destabilize the lowest unoccupied molecular orbital (LUMO) in **3** and also cause a slight destabilization of the H-1. This behaviour may be ascribed to the resonance effect of the ion pairs of the chlorine atoms, which destabilize the frontier MO. The latter results in the enhancement of the energy difference between H-1 and LUMO of **3** and thus a relative shift towards the blue of the lowest energy band compared with complex **1**.

Fig. 9 Relative energy diagram of the frontier molecular orbitals for **1** (on the left) and **3** (on the right). The zero is set on the HOMO energy. Note that the Cl-atoms in complex **3** are shown in light green.

Thermal stability of Zn(salphenazine)s

The thermal stability of Zn(salphenazine) complexes **1-7** has been examined by thermogravimetric analysis (TGA) under a nitrogen atmosphere (Table 1). All complexes show high thermal stability, the decomposition temperature ranges from 410°C (for complex **4**) to 520°C (for complex **2**). Comparing the di-substituted complexes **5** and **7** with the tetra-substituted complexes **1** and **4**, a higher thermal stability for the di-substituted systems was observed. In the case of complexes **1-4** (tetra-substituted ones), replacing the R¹ and R² substituent from Br to tBu, Cl or F leads to a significant increase in the decomposition temperature (*T_d*) from 410°C to up to 520°C. No glass transition temperature (*T_g*) was observed in the differential scanning calorimetric experiments (DSC) done for complexes **1-7**.

Table 1 Thermal degradation (*T_d*) data for complexes **1-7**.

Complex	R ¹	R ²	<i>T_d</i> (°C)
1	tBu	tBu	470
2	F	F	520
3	Cl	Cl	480
4	Br	Br	410
5	H	tBu	440
6	H	allyl	480
7	H	Br	440

Preparation of a smOSC based on Zn(salphenazine) **1**

Zn(salphenazine) complex **1** has the highest solubility among all the compounds reported herein and has relative good thermal stability (*vide infra*). At the same time, the spectroscopic properties of **1** display optimal characteristics to be donors in the production of relatively efficient smOSC and therefore this complex was selected for the preparation of a photovoltaic device.

One of the most important requisites for the correct operation of an OSC and the production of a photocurrent is the establishment of an adequate energy gap between the LUMO of the donor (i.e., Zn(salphenazine) complex **1**) and the acceptor (C₆₀) LUMO. The photogenerated electron-hole pair (exciton) is bound by a Coulombic force, which is of the order of 0.3 eV.²⁷ In order to successfully separate the charges, the general process requires excitons to travel to the donor-acceptor interface where the difference in donor and acceptor LUMO levels must exceed the Coulombic attraction force ($\Delta E_{\text{LUMO}} > 0.3$ eV). Energy values of the HOMO and LUMO for complex **1** have thus been calculated using differential pulse voltammetry (DPV), and absorption and emission spectroscopy. DPV of **1** was recorded in degassed acetonitrile (ACN) with 0.1 M tetrabutylammonium hexafluorophosphate (TBAP) as supporting electrolyte and all the potentials were referenced to the ferrocenyl/ferrocene (Fc^{+/0}/Fc) couple. Two reversible, anodic waves (confirmed by cyclic voltammetry, see ESI†) with *E_{ox}* at 0.852 V and 1.01 V were observed; both of them are attributed to the oxidation of the salphenazine ligand (Fig. 10A).

To determine the energy level of the HOMO, the following equation²⁸ was used (eq. 1)

$$E_{\text{HOMO}} = -(1.4 \pm 0.1) \times (qV_{\text{CV}}) - (4.6 \pm 0.08) \text{ eV} \quad (\text{eq. 1})$$

where *V_{CV}* corresponds to *E_{ox}* of complex **1**. The HOMO level of **1** was estimated to be −5.27 eV. From the intersection point between the normalized absorption and emission curves it is possible to extract the energy gap between HOMO and LUMO and consequently obtain the LUMO energy value of complex **1**. Figure 10B shows that the intersection point is at 560 nm, which corresponds to 2.21 eV (in good agreement with the DFT

calculated value, *vide infra*) and the LUMO level is -3.05 eV. By comparison with the LUMO value of C_{60} (-3.5 eV)²⁹ an OSC device based on complex **1** would display an acceptable ΔE_{LUMO} between donor and acceptor.

Fig. 10 (A) Differential pulse voltammetry for **1** vs Fc^+/Fc recorded in degassed ACN. (B) Normalized absorption (blue) and emission (light blue) spectra in ACN.

The devices were fabricated by spin coating a 1 mg/ml solution of Zn(salphenazine) **1** directly onto UV/O₃ treated indium tin oxide (ITO) (2000 rpm, 1min, ~ 10 nm thick), followed by the evaporation of C_{60} (40 nm), BCP (10 nm), and Al (100 nm), with devices having an active area of 0.09 cm^2 . The device was studied in the dark and under standard conditions (A.M 1.5 G solar spectrum, 100 mW cm^{-2}), and the current-voltage curves (J-V curve) of the **1**: C_{60} device are reported in Figure 12. The dark curve showed typical behaviour, with very low current in negative bias, with current being generated under forward bias at 0.5 V . From the dark curve we calculated the shunt resistance at short circuit to be $2 \times 10^6 \text{ ohm cm}^2$, and the series resistance at high forward bias to be 6.7 ohm cm^2 . The value of the shunt resistance is relatively high, which suggests that the leakage current is not too significant, even without an electron blocking layer. The series resistance on the other hand is rather high and contributes to the low fill factor (FF) of the devices. Under 1 Sun conditions the device recorded a power conversion efficiency (PCE) of 0.35%, which is calculated using the following equation (eq. 2):

$$\text{PCE} = (V_{\text{OC}} \times J_{\text{SC}} \times \text{FF}) / P_{\text{in}} \quad (\text{eq. 2})$$

Here, V_{OC} stands for the open-circuit voltage, J_{SC} is the current density at short-circuit and P_{in} is the incident power of the lamp. While this efficiency is not yet competitive compared to known systems,⁷⁻¹⁴ it nonetheless demonstrates the potential of this new class of compounds. In particular, the V_{OC} of the device was 0.65 V , which is acceptable but can be improved through modification of the HOMO level of donor. The FF was low due to the aforementioned high series resistance together with a strong voltage dependent current generation. In order to improve the FF, directly evaporating complex **1** could be a good strategy compared with the solution-process approach. The biggest limitation of the device was the J_{SC} , which was very low; the reason for this behavior is the modest extinction coefficient ϵ value of **1** together with the thin nature of the film employed. Increasing the thickness of the donor layer will improve absorption but due to the apparent low exciton-diffusion length, further improvements in J_{SC} are not possible. Thus a better design at the molecular level is needed to reduce the overlap between donor and acceptor moieties (extend π -conjugation) and to increase the ϵ value of the donor molecules.

Fig. 11 J-V curve for the devices comprising of ITO/**1**/ C_{60} /BCP/Al.

An approach to improve the photocurrent and the relative efficiency of this complex would be to utilize a bulk heterojunction architecture,^{14a} which maximizes the interfacial area between donor and acceptor as well as allowing thicker films to be employed. A possible advantage of Zn(salphen) complexes in this regard is their ability to self-assemble creating well-ordered large domains which would ideally be surrounded by an acceptor-matrix.³⁰

Conclusions

In summary, a new class of Zn(II) Schiff base complexes incorporating a phenazine unit in the backbone has been developed. Salphenazine complexes show interesting spectroscopic properties compared to typical salen and salphen complexes while remaining easily synthesized and tuneable. From the experimental and theoretical UV-Vis data the absorption bands have been assigned to π - π^* transitions which are directly influenced by the type of substituents present in the salphenazine scaffold. Therefore, by a judicious choice of these groups, it is

possible to obtain systems with desired spectroscopic properties.

Zn(salphenazine) complexes have also shown to have potential application in smOSCs due to their high stability and adequate electronic properties against the acceptor C₆₀. Even though the efficiency of the device is not competitive yet, Zn(salphenazine)s show the synthetic potential for significant improvement based on the modular construction of these photo-active complexes.

Experimental

General comments

All chemicals were commercial available and were used as received. ¹H NMR and ¹³C{¹H} NMR spectra were recorded on Bruker Avance 400 MHz Ultrashield NMR spectrometers at 297 K. Chemical shifts are reported in ppm relative to tetramethylsilane ($\delta = 0$ ppm) as an internal standard. Mass analyses were carried out by the Mass Spectrometry Unit at the Institute of Chemical Research of Catalonia (ICIQ, Spain) using either DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile) or pyrene as matrix. Crystallographic analyses were also performed at ICIQ by the X-ray crystallographic unit. Elemental analyses were determined by the Elemental Analysis Unit of the University of Santiago de Compostela, Spain. UV-Vis spectra were acquired on a Shimadzu UV-1800 spectrophotometer. Fluorescence spectroscopy was performed on an AMINCO Bowman series 2 luminescence spectrometer. Acetonitrile, *N,N*-dimethylformamide (DMF), tetrahydrofuran (THF) and toluene used for UV-Vis and the DPV experiment were dried by using a solvent purification system (SPS) from Innovative Technology. The complexes **10**,^{23a} **11**³¹ and **12**³² were prepared using previously reported procedures. For all complexes that contain solvent impurities in the microanalysis samples, copies of the ¹H NMR spectra are presented in the ESI†.

DFT calculations

All calculations were performed with the Gaussian 09 (G09) program package³³ employing the DFT method with Becke's three-parameter hybrid functional³⁴ and Lee–Yang–Parr's gradient-corrected correlation functional (B3LYP).³⁵ The LanL2DZ basis set³⁶ and effective core potential were used for the Zn atom, and the split-valence 6-311G** basis set³⁷ was applied for all other atoms. Geometry optimizations of the complexes were performed without any constraint, and the nature of all stationary points was confirmed by normal-mode analysis. Non-equilibrium TDDFT calculations produced singlet excited states employing the DFT method with the hybrid functional of Truhlar and Zhao (M06),³⁹ using the conductor like polarizable continuum model method (CPCM)⁴⁰ with THF as solvent. Eighty singlet excited states were determined starting from optimized geometries of **1** and **3**. Electronic distributions and localizations of the singlet excited states were visualized using the electron density difference maps (EDDMs).⁴¹ GaussSum 2.25⁴² was used for singlet EDDMs calculations and for simulation of the electronic spectra.

Differential pulse voltammetry

Differential pulse voltammetry (DPV) experiments were carried out using a CH Instruments 660c Electrochemical Workstation,

with a standard three-electrode setup utilizing a Pt disc working electrode, Pt wire working electrode and SCE reference electrode. A 0.1 M solution of tetrabutylammonium phosphate in DMSO was used as the background electrolyte. Cyclic voltammetry experiments were run under similar conditions.

Device fabrication

Devices were prepared on ITO substrates (5 ohm/square, Psiotech Ltd. U.K.). The substrates were cleaned by sonicating, firstly in acetone, followed by two cycles of sonication in 2-propanol, and then treated with UV/O₃ for 20 min. Thin films of the Zn(salphenazine) donor **1** were prepared by spin-coating a 1 mg/ml solution of the donor in CHCl₃ (filtered using a PTFE membrane, pore size = 0.2 μ m) at a rate of 2000 rpm for 1 minute. Subsequently, the films were transferred to an evaporation chamber where the C₆₀ (40 nm, MER Corp., 99.9%), bathocuproine BCP (8 nm, Sigma Aldrich), and Al (100 nm, Sigma Aldrich) were deposited at a base pressure of 1×10^{-6} mbar. Device J-V curves were recorded using a 150 W solar simulator (Abet Technologies) at 1 sun conditions (AM 1.5 G, 100 mW/cm²).

Syntheses

Zn(salphenazine) complex (1): 2,3-diaminophenazine (103 mg, 0.49 mmol) was dissolved in DMSO (2 mL) and the mixture was heated to 95°C in order to dissolve the reagent. While stirring, to the heated solution was added a methanol solution (2 mL) of 3,5-*tert*-butyl-2-hydroxybenzaldehyde (230 mg, 0.75 mmol) and a methanol solution (1 mL) of Zn(OAc)₂·H₂O (88 mg, 0.40 mmol). The solution was stirred for 18 h at 95°C, subsequently cooled to room temperature and the precipitate which had formed was filtered off, washed with methanol and dried under vacuum to yield a dark brown powder (44 mg, 12 %). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.41 (s, 2H; CH=N), 8.64 (s, 2H; ArH), 8.18–8.20 (m, 2H; ArH), 7.87–7.93 (m, 2H; ArH), 7.41 (d, 2H, ⁴J_{HH} = 2.7 Hz; ArH), 7.39 (d, 2H, ⁴J_{HH} = 2.7 Hz; ArH), 1.51 (s, 9H; tBu), 1.32 (s, 9H; tBu); Due to the low solubility of **1** a proper ¹³C NMR analysis was not possible; MALDI(+): *m/z* = 704.5 [M]⁺ (calcd. 704.31); UV-Vis (*c* = 0.25 mg in 20 mL THF): $\lambda_{\max}$ (ϵ) = 231 nm (43107 mol⁻¹·m³·cm⁻¹), $\lambda_{\max}$ (ϵ) = 257 nm (42508 mol⁻¹·m³·cm⁻¹), $\lambda_{\max}$ (ϵ) = 328 nm (37445 mol⁻¹·m³·cm⁻¹), $\lambda_{\max}$ (ϵ) = 384 nm (28709 mol⁻¹·m³·cm⁻¹), $\lambda_{\max}$ (ϵ) = 516 nm (34357 mol⁻¹·m³·cm⁻¹); elemental analysis calcd. (%) for C₄₂H₄₈N₄O₂Zn·2H₂O: C 68.80, H 7.01, N 7.64; found: C 68.82, H 7.27, N 7.55.

Zn(salphenazine) complex (2): This compound was prepared in a similar manner to complex **1** using 2,3-diaminophenazine (108 mg, 0.51 mmol), 3,5-difluorosalicylaldehyde (162 mg, 1.03 mmol) and Zn(OAc)₂·H₂O (116 mg, 0.53 mmol). After cooling to room temperature the complex was precipitated by further addition of methanol to yield a red powder (185 mg, 66 %). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.37 (s, 2H; CH=N), 8.66 (s, 2H; ArH), 8.23–8.25 (m, 2H; ArH), 7.96–7.98 (m, 2H; ArH), 7.34–7.40 (m, 2H; ArH), 7.24–7.27 (m, 2H; ArH); ¹⁹F NMR (400 MHz, DMSO-*d*₆): δ = -129.96 (d, 2F, ³J_{HF} = 11.4 Hz; ArF), -130.66 (dd, 2F, ³J_{HF} = 8.8 Hz, ³J_{HF} = 8.8 Hz; ArF); Due to the low solubility of **2** a proper ¹³C NMR analysis was not possible; MALDI(+): *m/z* = 552.1 [M]⁺ (calcd. 552.02), 1108.2 [2M]⁺ (calcd. 1108.3); UV-Vis (*c* = 0.25 mg in 20 mL THF): $\lambda_{\max}$ (ϵ) = 277 nm (74112 mol⁻¹·m³·cm⁻¹), $\lambda_{\max}$

(ϵ) = 365 nm (15685 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 483 nm (22177 mol⁻¹·m³·cm⁻¹); elemental analysis calcd. (%) for C₂₆H₁₂F₄N₄O₂Zn·MeOH·2/3DMSO: C 52.37, H 2.82, N 9.05, S 3.45; found: C 52.29, H 2.94, N 8.90, S 3.47. The presence of DMSO and MeOH in the microanalysis sample was also supported by ¹H NMR.

Zn(salphenazine) complex (3): This compound was prepared in a similar manner to complex **1** using 2,3-diaminophenazine (93.4 mg, 0.44 mmol), 3,5-dichlorosalicylaldehyde (178 mg, 0.93 mmol) and Zn(OAc)₂·H₂O (109 mg, 0.5 mmol). After cooling to room temperature the complex was precipitated by addition of extra methanol to yield an orange powder (200 mg, 73 %). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.34 (s, 2H; CH=N), 8.64 (s, 2H; ArH), 8.23-8.25 (m, 2H; ArH), 7.95-7.98 (m, 2H; ArH), 7.64 (d, 2H, ⁴*J*_{HH} = 2.9 Hz; ArH), 7.62 (d, 2H, ⁴*J*_{HH} = 2.9 Hz; ArH); Complex **3** was too insoluble for a proper ¹³C NMR analysis; MALDI(+): *m/z* = 617.8 [M]⁺ (calcd. 617.9), 1237.6 [2M]⁺ (calcd. 1237.79); UV-Vis (*c* = 0.25 mg in 20 mL THF): λ_{max} (ϵ) = 256 nm (45424 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 316 nm (31863 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 366 nm (20328 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 484 nm (30383 mol⁻¹·m³·cm⁻¹); elemental analysis calcd. (%) for C₄₂H₄₈N₄O₂Zn·H₂O·DMSO: C 46.99, H 2.82, N 7.83; found: C 46.40, H 2.27, N 7.50. The presence of DMSO in the microanalysis sample was also supported by ¹H NMR analysis.

Zn(salphenazine) complex (4): This compound was prepared in a similar manner to **1** using 2,3-diaminophenazine (107 mg, 0.51 mmol), 3,5-dibromosalicylaldehyde (285 mg, 1.02 mmol) and Zn(OAc)₂·H₂O (132 mg, 0.60 mmol). After cooling to room temperature the complex was precipitated by addition of extra methanol to yield a dark orange powder (295 mg, 73 %). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.32 (s, 2H; CH=N), 8.63 (s, 2H; ArH), 8.22-8.25 (m, 2H; ArH), 7.95-7.97 (m, 2H; ArH), 7.84 (d, 2H, ⁴*J*_{HH} = 2.5 Hz; ArH), 7.62 (d, 2H, ⁴*J*_{HH} = 2.5 Hz; ArH); Complex was too insoluble for a proper ¹³C NMR analysis; MALDI(+): *m/z* = 797.8 [M]⁺ (calcd. 797.69), 1595.4 [2M]⁺ (calcd. 1595.38); UV-Vis (*c* = 0.25 mg in 20 mL THF): λ_{max} (ϵ) = 233 nm (47110 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 256 nm (61100 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 317 nm (37110 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 368 nm (24770 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 485 nm (34220 mol⁻¹·m³·cm⁻¹); elemental analysis calcd. (%) for C₂₆H₁₂Br₂N₄O₂Zn: C 39.16, H 1.52, N 7.03; found: C 39.19, H 1.74, N 6.93.

Zn(salphenazine) complex (5): This compound was prepared in a similar manner to complex **1** using 2,3-diaminophenazine (108 mg, 0.51 mmol), 3-tert-butyl-2-hydroxybenzaldehyde (183 mg, 1.03 mmol) and Zn(OAc)₂·H₂O (114 mg, 0.52 mmol). After cooling to room temperature the complex was precipitated by further addition of methanol to yield a dark brown powder (62 mg, 20 %). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.35 (s, 2H; CH=N), 8.61 (s, 2H; ArH), 8.20-8.22 (m, 2H; ArH), 7.92-7.94 (m, 2H; ArH), 7.42 (d, 2H, ³*J*_{HH} = 7.8 Hz, ⁴*J*_{HH} = 1.7 Hz; ArH), 7.30 (d, 2H, ³*J*_{HH} = 7.8 Hz, ⁴*J*_{HH} = 1.7 Hz; ArH), 6.52 (dd, 2H, ³*J*_{HH} = 7.8, ³*J*_{HH} = 7.8 Hz, ArH), 1.49 (s, 9H; tBu); Complex **5** was too insoluble for a proper ¹³C NMR analysis; MALDI(+): *m/z* = 592.3 [M]⁺ (calcd. 592.18); UV-Vis (*c* = 0.22 mg in 20 mL THF): λ_{max} (ϵ) = 228 nm (32067 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 255 nm (36994 mol⁻¹·m³·cm⁻¹),

λ_{max} (ϵ) = 326 nm (33442 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 375 nm (26488 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 501 nm (36820 mol⁻¹·m³·cm⁻¹); elemental analysis calcd. (%) for C₃₄H₃₂N₄O₂Zn·½DMSO·½MeOH·H₂O: C 63.91, H 5.89, N 8.40; found: C 64.07, H 5.56, N 8.78. The presence of DMSO and MeOH in the microanalysis sample was also supported by ¹H NMR.

Zn(salphenazine) complex (6): This compound was prepared in a similar manner to complex **1** using 2,3-diaminophenazine (146 mg, 0.69 mmol), 3-allyl-salicylaldehyde (236 mg, 1.46 mmol) and Zn(OAc)₂·H₂O (156 mg, 0.71 mmol). After cooling to room temperature the complex was precipitated by addition of methanol to yield a reddish brown powder (233 mg, 60 %). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 9.28 (s, 2H; CH=N), 8.56 (s, 2H; ArH), 8.19-8.22 (m, 2H; ArH), 7.91-7.94 (m, 2H; ArH), 7.42 (d, 2H, ³*J*_{HH} = 8.0 Hz, ⁴*J*_{HH} = 1.7 Hz; ArH), 7.23 (d, 2H, ³*J*_{HH} = 7.0 Hz, ⁴*J*_{HH} = 1.8 Hz; ArH), 6.52 (d, 2H, ³*J*_{HH} = 7.0, ³*J*_{HH} = 8.0 Hz; ArH), 6.14-6.22 (m, 2H; allyl-H), 5.13-5.18 (m, 2H; allyl-H), 5.01-5.03 (m, 2H; allyl-H), 3.44 (d, 4H, ³*J*_{HH} = 6.8 Hz; allyl-H); Complex was too insoluble for a proper ¹³C NMR analysis; MALDI(+): *m/z* = 560.1 [M]⁺ (calcd. 560.12), 1124.2 [2M]⁺ (calcd. 1124.23); UV-Vis (*c* = 0.25 mg in 20 mL THF): λ_{max} (ϵ) = 224 nm (36150 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 255 nm (44000 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 322 nm (31584 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 371 nm (23811 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 491 nm (32830 mol⁻¹·m³·cm⁻¹); elemental analysis calcd. (%) for C₃₂H₂₄N₄O₂Zn·MeOH·H₂O: C 64.76, H 4.94, N 9.15; found: C 64.87, H 4.73, N 9.40. The presence of MeOH in the microanalysis sample was also supported by ¹H NMR.

Zn(salphenazine) complex (7): This compound was prepared in a similar manner to complex **1** using 2,3-diaminophenazine (107 mg, 0.51 mmol), 3-bromo-salicylaldehyde (215 mg, 1.07 mmol) and Zn(OAc)₂·H₂O (132 mg, 0.60 mmol). After cooling to room temperature the complex was precipitated by further addition of methanol to yield an orange powder (146 mg, 45 %). ¹H NMR (400 MHz, DMSO-*d*₆): δ = 9.36 (s, 2H; CH=N), 8.66 (s, 2H; ArH), 8.22-8.25 (m, 2H; ArH), 7.95-7.97 (m, 2H; ArH), 7.75 (d, 2H, ³*J*_{HH} = 7.6 Hz, ⁴*J*_{HH} = 1.8 Hz; ArH), 7.61 (d, 2H, ³*J*_{HH} = 7.6 Hz, ⁴*J*_{HH} = 1.8 Hz; ArH), 6.53 (dd, 2H, ³*J*_{HH} = 7.6 Hz, ³*J*_{HH} = 7.6 Hz, ArH); Complex **7** was too insoluble for a proper ¹³C NMR analysis; MALDI(+): *m/z* = 639.9 [M]⁺ (calcd. 639.87), 1279.8 [2M]⁺ (calcd. 1279.75); UV-Vis (*c* = 0.25 mg in 20 mL THF): λ_{max} (ϵ) = 234 nm (34887 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 253 nm (42152 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 321 nm (33094 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 367 nm (24573 mol⁻¹·m³·cm⁻¹), λ_{max} (ϵ) = 482 nm (33632 mol⁻¹·m³·cm⁻¹); elemental analysis calcd. (%) for C₂₆H₁₄Br₂N₄O₂Zn·H₂O: C 47.49, H 2.45, N 8.52; found: C 47.59, H 2.36, N 8.22.

Zn(salphenazine) complex (8): This compound was prepared in a similar manner to complex **1** using 2,3-diaminophenazine (109 mg, 0.52 mmol), 2-hydroxy-1-naphthaldehyde (187 mg, 1.04 mmol) and Zn(OAc)₂·H₂O (119 mg, 0.54 mmol). After cooling to room temperature the precipitate which formed, was filtered off and washed with methanol to yield a brown powder (164 mg, 54 %). ¹H NMR (500 MHz, DMSO-*d*₆): δ = 10.05 (s, 2H; ArH), 8.76 (s, 2H; CH=N), 8.64 (d, 2H, ³*J*_{HH} = 8.5 Hz; ArH), 8.22-8.24 (m, 2H; ArH), 7.92-7.94 (m, 2H; ArH), 7.88 (d, 2H, ³*J*_{HH} = 9.3 Hz;

ArH), 7.74 (d, 2H, $^3J_{\text{HH}} = 7.9$ Hz, $^4J_{\text{HH}} = 1.1$ Hz; ArH), 7.54 (d, 2H, $^3J_{\text{HH}} = 7.9$ Hz, $^4J_{\text{HH}} = 1.2$ Hz; ArH), 7.30 (d, 2H, $^3J_{\text{HH}} = 7.4$, $^4J_{\text{HH}} = 1.1$ Hz, ArH), 7.02 (d, 2H, $^3J_{\text{HH}} = 9.1$ Hz; ArH); Complex **8** was too insoluble for a proper ^{13}C NMR analysis; MALDI(+): $m/z = 580.3$ $[\text{M}]^+$ (calcd. 580.09); UV-Vis ($c = 0.20$ mg in 20 mL THF): $\lambda_{\text{max}}(\epsilon) = 248$ nm ($56802 \text{ mol}^{-1} \cdot \text{m}^3 \cdot \text{cm}^{-1}$), $\lambda_{\text{max}}(\epsilon) = 322$ nm ($18520 \text{ mol}^{-1} \cdot \text{m}^3 \cdot \text{cm}^{-1}$), $\lambda_{\text{max}}(\epsilon) = 356$ nm ($14414 \text{ mol}^{-1} \cdot \text{m}^3 \cdot \text{cm}^{-1}$), $\lambda_{\text{max}}(\epsilon) = 428$ nm ($23622 \text{ mol}^{-1} \cdot \text{m}^3 \cdot \text{cm}^{-1}$), $\lambda_{\text{max}}(\epsilon) = 522$ nm ($33424 \text{ mol}^{-1} \cdot \text{m}^3 \cdot \text{cm}^{-1}$); elemental analysis calcd. (%) for $\text{C}_{34}\text{H}_{20}\text{N}_4\text{O}_2\text{Zn} \cdot 2\text{H}_2\text{O}$: 66.08, H 3.91, N 9.07; found: C 65.61, H 3.73, N 9.48.

Zn₈(salphenazine)₄ cluster complex (9): 2,3-diaminophenazine (90 mg, 0.42 mmol) was dissolved in DMSO (1.5 mL) and the mixture was heated to 100°C in order to dissolve the reagent. While stirring, to the heated solution was added a DMSO solution (1 mL) of 2,3-dihydroxy-benzaldehyde (130 mg, 0.94 mmol) and a methanol solution (1 mL) of $\text{Zn}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (193 mg, 0.87 mmol). The reaction mixture was stirred for 2 h at 100°C, and subsequently cooled to room temperature. A further amount of methanol was added and the precipitate which formed was filtered off. The solid that was obtained was recrystallized from hot DMF/pyridine to yield a brown powder which was washed thoroughly with MeOH and dried (59 mg, 23 %). ^1H NMR (400 MHz, DMSO- d_6): $\delta = 9.50$ (s, 4H; CH=N), $\delta = 9.10$ (s, 4H; CH=N), 8.87 (s, 4H; ArH), 8.62 (s, 4H; ArH), 8.24-8.27 (m, 8H; ArH), 7.94-8.10 (m, 8H; ArH), 6.97 (d, 4H, $^3J_{\text{HH}} = 7.3$ Hz; ArH), 6.68 (d, 4H, $^3J_{\text{HH}} = 7.7$ Hz; ArH), 6.55-6.59 (m, 8H; ArH), 6.43 (d, 4H, $^3J_{\text{HH}} = 7.6$ Hz; ArH), 5.96-6.02 (m, 4H; ArH); Complex **9** was too insoluble for a proper ^{13}C NMR analysis; MALDI(+): $m/z = 2308.1$ $[\text{M}]^+$ (calcd. 2308.83); UV-Vis ($c = 0.65$ mg in 20 mL THF): $\lambda_{\text{max}}(\epsilon) = 413$ nm ($94263 \text{ mol}^{-1} \cdot \text{m}^3 \cdot \text{cm}^{-1}$); elemental analysis calcd. (%) for $\text{C}_{104}\text{H}_{56}\text{N}_{16}\text{O}_{16}\text{Zn}_8 \cdot 3\text{pyr} \cdot 3\text{H}_2\text{O} \cdot \frac{1}{4}\text{MeOH}$: C 54.59, H 3.04, N 10.17; found: C 55.01, H 3.62, N 10.11. The presence of pyridine and MeOH in the microanalysis sample was supported by ^1H NMR. Please note that these octanuclear structures usually retain four water molecules (cf., Fig. 3)^{20a} coordinating to the outer Zn centres; the pyridine and MeOH molecules are thought to be associated via H-bonding to the water ligands.

X-ray crystallography

General: The measured crystals were stable under atmospheric conditions; nevertheless they were treated under inert conditions and were immersed in perfluoropoly-ether as a protecting oil for manipulation. Data collection: measurements were made on a Bruker-Nonius diffractometer equipped with an APEX 2 4K CCD area detector, an FR591 rotating anode with MoK α radiation, Montel mirrors and a Kryoflex low temperature device ($T = -173$ °C). Full-sphere data collection was used with ω and ϕ scans. Programs used: data collection Apex2 V2011.3 (Bruker-Nonius 2008), data reduction Saint+Version 7.60A (Bruker AXS 2008) and absorption correction SADABS V. 2008–1 (2008). Structure solution: SHELXTL version 6.10 (Sheldrick, 2000)⁴³ was used. Structure refinement: SHELXTL-97-UNIX VERSION.

Crystallographic details for complex 1·3DMSO: $\text{C}_{48}\text{H}_{66}\text{N}_4\text{O}_5\text{S}_3\text{Zn}$, $M_r = 940.60$, triclinic, $P-1$, $a = 9.8772(5)$ Å, $b = 13.4186(6)$ Å, $c = 19.0545(8)$ Å, $\alpha = 85.820(3)^\circ$, $\beta = 75.934(2)^\circ$, $\gamma = 85.146(2)^\circ$, $V =$

$2437.36(19)$ Å³, $Z = 2$, $\rho = 1.282 \text{ mg} \cdot \text{M}^{-3}$, $\mu = 0.680 \text{ mm}^{-1}$, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $F(000) = 1000$, crystal size = $0.50 \times 0.20 \times 0.10$ mm, $\theta(\text{min}) = 1.53^\circ$, $\theta(\text{max}) = 36.57^\circ$, 21580 reflections collected, 21580 reflections unique ($R_{\text{int}} = 0.0544$), GoF = 1.028, $R_1 = 0.0460$ and $wR_2 = 0.1070$ [$I > 2\sigma(I)$], $R_1 = 0.0783$ and $wR_2 = 0.1221$ (all indices), min/max residual density = $-0.765/1.056$ [e·Å⁻³]. Completeness to $\theta(36.57^\circ) = 0.896\%$. The structure has been deposited at the CCDC with reference number 949796 and is a bis-solvate; it contains two co-crystallized DMSO molecules alongside one coordinating one.

Crystallographic details for complex 5·3DMSO: $\text{C}_{40}\text{H}_{50}\text{N}_4\text{O}_5\text{S}_3\text{Zn}$, $M_r = 828.39$, monoclinic, $P2(1)/c$, $a = 16.9962(6)$ Å, $b = 13.2017(5)$ Å, $c = 18.0315(7)$ Å, $\alpha = 90^\circ$, $\beta = 94.076(2)^\circ$, $\gamma = 90^\circ$, $V = 4035.7(3)$ Å³, $Z = 4$, $\rho = 1.363 \text{ mg} \cdot \text{M}^{-3}$, $\mu = 0.812 \text{ mm}^{-1}$, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $F(000) = 1744$, crystal size = $0.40 \times 0.15 \times 0.02$ mm, $\theta(\text{min}) = 1.20^\circ$, $\theta(\text{max}) = 36.36^\circ$, 73442 reflections collected, 18952 reflections unique ($R_{\text{int}} = 0.1023$), GoF = 0.976, $R_1 = 0.0551$ and $wR_2 = 0.1025$ [$I > 2\sigma(I)$], $R_1 = 0.1324$ and $wR_2 = 0.1309$ (all indices), min/max residual density = $-0.708/0.717$ [e·Å⁻³]. Completeness to $\theta(36.36^\circ) = 0.966\%$. The structure has been deposited at the CCDC with reference number 949797 and is a bis-solvate; it contains two co-crystallized DMSO molecules alongside one coordinating one. One of the co-crystallized DMSO molecules is disordered over two positions with a relative occupancy ratio of 77:23.

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Notes and references

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