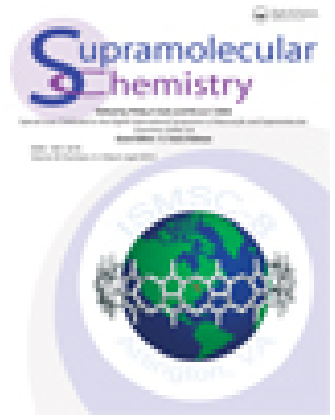

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Yujin Lee[ab], Hyo Geun Koo[ab], Seung Pyo Jang[ab], Alan B. Erdmann[a], Samantha S. Vernetti[a], Cheal Kim[b] & Roger G. Harrison[a]

[a] Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, USA

[b] Department of Fine Chemistry, Seoul National University of Science & Technology, , Seoul 139-743, Republic of Korea

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[a]*Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602, USA;* [b]*Department of Fine Chemistry, Seoul National University of Science & Technology, Seoul 139-743, Republic of Korea*

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The synthesis, spectroscopic characterisation, conformational switching and fluorescence quenching efficiency of a resorcinarene-based cavitand containing Zn-salen (**Zn-Cav**) are reported. Synthesis of **Zn-Cav** was accomplished by the condensation of a quinoxaline derivatised with Zn-salen and a resorcinarene-based cavitand containing three quinoxalines. ^{1}H NMR spectroscopy confirmed that in DMSO, chloroform and acetone **Zn-Cav** resides in the vase conformation. The molecular geometry of **Zn-Cav** selectively changes from vase to kite under acidic conditions. Detection by fluorescence quenching of nitro-containing molecules, such as 4-nitrotoluene, 2,4-dinitrotoluene and 2,3-dimethyl-2,3-dinitrobutane was explored by spectrofluorimetry. It was found that the fluorescence of **Zn-Cav** is efficiently quenched by nitroaromatic compounds.

Keywords: molecular recognition; fluorescence quenching; dinitrotoluene

Introduction

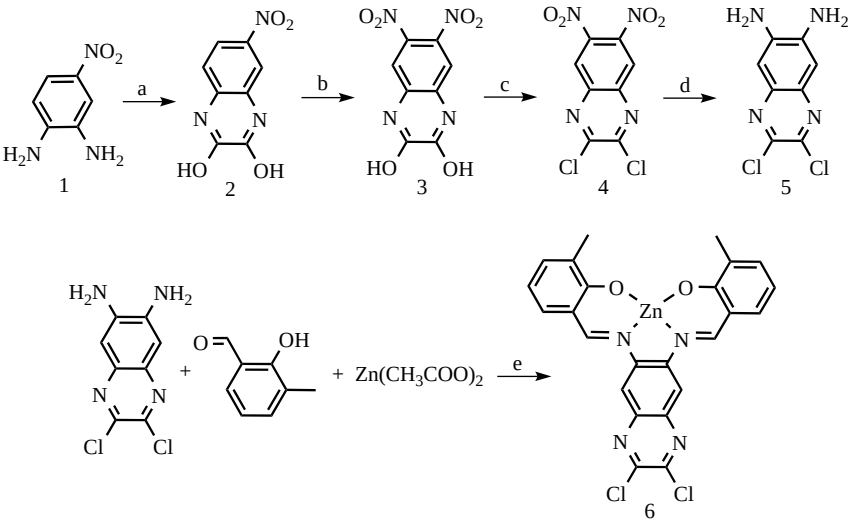
The design of molecular receptors, combining guest binding and detection, continues to be an important area of research. Resorcinarene-based cavitands have become established as one of the classes of molecular receptors. They have a cavity surrounded by four binding regions, which may act in cooperative guest binding. They can also be functionalised with groups that elongate their cavities and result in enclosed cavities. Their ability to have groups attached to them has resulted in cavitands with hydrogen bonding moieties, chiral groups and metal ions (*1*).

Resorcinarenes have cavities that can be switched between open and enclosed. Conformational switching can be induced by changes in temperature (*2*) and pH (*3*), with the kite conformation being preferred at low temperatures and low pH values. The development of molecular sensors, receptors and machines is based on the switching between the vase conformation, with a deep cavity for guest binding and the kite conformation with a flat surface (*4*). Nuclear magnetic resonance spectroscopy is usually used to monitor the recognition of guest binding to host and molecular switching between kite and vase (*5*).

Cavitands, with their molecular recognition sites, have shown the ability to bind a variety of molecules (*6*). Although ^{1}H NMR is an excellent technique to monitor host–guest interactions, it is not feasible for the monitoring of large numbers of samples. Molecules that show a change in fluorescence are used extensively to detect molecules, due to fluorescence being very sensitive (*7*). Explosives containing nitro groups and the volatile additive 2,3-dimethyl-2,3-dinitrobutane (DMNB) need to be detected due to their use in bombs and as an explosive additive. Detecting these by fluorescence sensors would potentially give a quick response to their presence (*8*). Zn-salen complexes have optical properties, such as fluorescence, that might be useful in sensor materials (*9*). In fact, their use in detecting explosive type compounds has been initiated (*10*). Cavitands functionalised with fluorescent molecules might be aided by their molecular recognition sites in the detection of nitro-containing explosives.

In this work, we present the synthesis and characterisation of a resorcinarene-based cavitand (**Zn-Cav**) that contains one Zn-salen and three other quinoxaline groups. There is one previous example of a resorcinarene that contains a Zn-salen moiety; it was successfully used in catalysis (*11*). Our molecule is synthesised by the condensation of a specially prepared Zn-salen quinoxaline with a resorcinarene that contains three quinoxaline arms. ^{1}H NMR spectra confirm that **Zn-Cav** is in the vase conformation in DMSO, chloroform and acetone, as its methine protons appear around 5.5 ppm. **Zn-Cav** absorbs visible light and fluoresces with a high quantum yield. It has several molecular recognition properties: (1) a cavity provided from the vase conformation of the cavitand; (2) a Zn^{2+} that provides a binding site for Lewis base guest molecules and (3) a Zn-salen group, which has excellent

*Corresponding author. Email: roger_harrison@byu.edu



Scheme 1. Synthesis of Zn-salen quinoxaline. (a) Oxalic acid (1.5 equiv.), H_2O, HCl, 115°C, 21 h. (b) KNO_3, H_2SO_4, 0°C for 1 h and then at r.t. for 18 h. (c) $POCl_3$, N-N-dimethylaniline, 110°C, 3 h. (d) $SnCl_2$, HCl, EtOH, r.t., 1 h. (e) MeOH, r.t., 18 h.

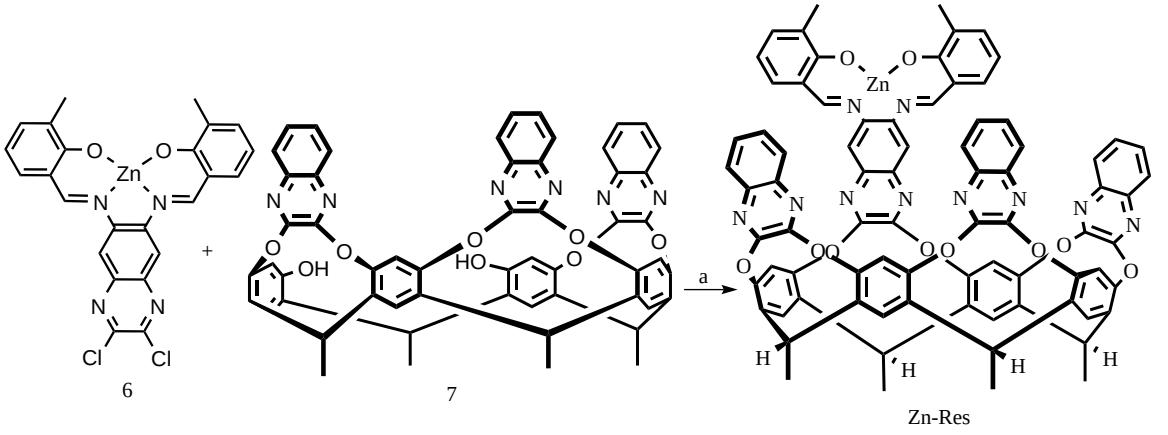
photophysical properties. It was found that the fluorescence of **Zn-Cav** was efficiently quenched by 4-nitrotoluene (NT), 2,4-dinitrotoluene (DNT) and DMNB.

Result and discussion

The synthesis of **Zn-Cav** required making a Zn-salen group and bonding it to a resorcinarene with one open bridging site. The Zn-salen group was prepared by first synthesising diaminodichloroquinoxaline (Scheme 1). To make this quinoxaline, nitrodiaminobenzene was reacted with oxalic acid to form dihyroxynitroquinoxaline, after which another nitro group was added, the hydroxyl groups were exchanged for chlorines and the nitro groups were reduced to amines. With the amino groups next to each other, the molecule was condensed with two equivalents of 2-hydroxy-3-methylbenzaldehyde and $Zn(CH_3COO)_2$ to form the Zn^{2+} containing dichloroquinoxaline (**6**). Molecule **6** absorbs light at 320 and 461 nm and fluoresces at 476 nm in DMSO with a quantum yield of 0.51.

The ^1H NMR of **6** shows six peaks, with the imine protons at 9.19 ppm. The hydroxyl proton is not present in the NMR spectrum and displaced when Zn^{2+} bonds, resulting in a neutral molecule. The structure of this molecule is predicted to be similar to a Zn-salen complex in the literature (*10*). In the solid state, the Zn is most likely positioned a little above the plane of the four coordinating atoms and is five coordinate, with its fifth coordination site occupied by O from a DMSO molecule. Thus, the Zn would be in a pseudosquare pyramidal geometry.

The Zn-salen-containing resorcinarene (**Zn-Cav**) was synthesised by bonding **6** to a resorcinarene with three quinoxaline groups (**7**) (Scheme 2). The resorcinarene with three quinoxaline groups was prepared by adding two



Scheme 2. Synthesis of **Zn-Cav**. (a) K_2CO_3, dry DMSO, 50°C, 48 h.

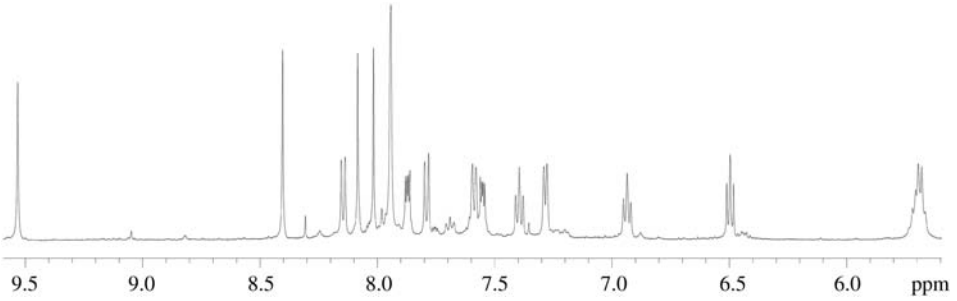


Figure 1. ^{1}H NMR spectrum of Zn-salen resorcinarene in DMSO. The aromatic region shows protons with 14 different chemical shifts. The methine proton from the foot comes at 5.7 ppm.

equivalents of dichloroquinoxaline to resorcinarene and then isolating it from the mixture (*12*). The addition of Zn-salen to the resorcinarene went as anticipated and the Zn-salen group closed the macrocycle. The ^{1}H NMR spectrum showed a multitude of peaks in the aromatic region (Figure 1). **Zn-Cav** has a mirror plane of symmetry bisecting the Zn and one of the quinoxaline arms opposite the Zn-salen. This results in 17 different proton resonances, 14 of which are in the aromatic region ranging from 6.5 to 9.5 ppm. Of major interest is the resonance for the methine proton on the foot of the resorcinarene, because it gives the conformation of the resorcinarene. This proton comes at 5.69 ppm in DMSO and thus the resorcinarene is in the vase conformation. Resorcinarenes in the vase form have methine protons that appear at around 5.5 ppm, whereas when in the kite form their resonances are upfield at around 4.0 ppm (*2b*, *13*). As with the Zn-salen, **Zn-Cav** absorbs visible light and fluoresces at a high quantum yield (Figure 2, Øem = 0.59). Its absorption bands at 320 and 458 nm and its emission band at 468 nm are all near to where they were for the Zn-salen and are thus not affected by the resorcinarene.

Although **Zn-Cav** resides in the vase conformation, it changes to the kite at low pH. In DMSO, chloroform and acetone, the methine resonances of **Zn-Cav** come at around 5.5 ppm and thus **Zn-Cav** has a vase conformation. However, acidifying a chloroform solution of **Zn-Cav** with trifluoroacetic acid at room temperature led to the methine peak moving from 5.35 to 4.00 ppm. This vase to kite conversion most likely arises as a result of the protonation of the basic quinoxaline N atoms, which when protonated repel each other due to their positive charge (*12*). Unlike in chloroform, lowering the pH of DMSO and acetone solutions did not cause the methine to change chemical shift.

Recognising the intense fluorescence of **Zn-Cav**, we tested its ability to act as a sensor for nitro-containing compounds. When a solution of **Zn-Cav** was exposed to 4-NT, the **Zn-Cav** emission peak at 480 nm was drastically reduced (Figure 3). This fluorescence quenching was not dependent on solvent and occurred in acetonitrile, chloroform and DMSO. Other nitro compounds, such as DMNB, also quenched the fluorescence of **Zn-Cav**. Plotting the diminishing fluorescence as a function of amount of nitro compound and calculating the slope, we obtained Stern–Volmer constants. The constants for NT and DNT with **Zn-Cav** were similar in magnitude and around 100 M^{-1} (4-NT: 107 M^{-1}, 2,4-DNT: 110 M^{-1}).

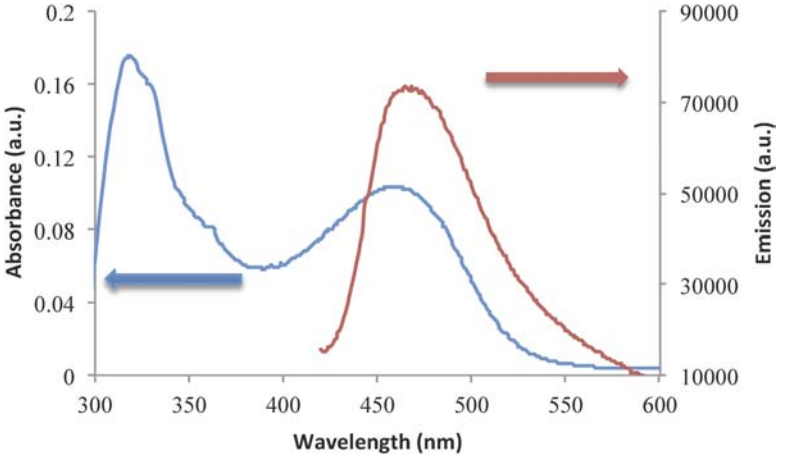


Figure 2. (Colour online) Absorption (left) and emission (right) spectra of **Zn-Cav**. The solvent was DMSO and the excitation was at 400 nm.

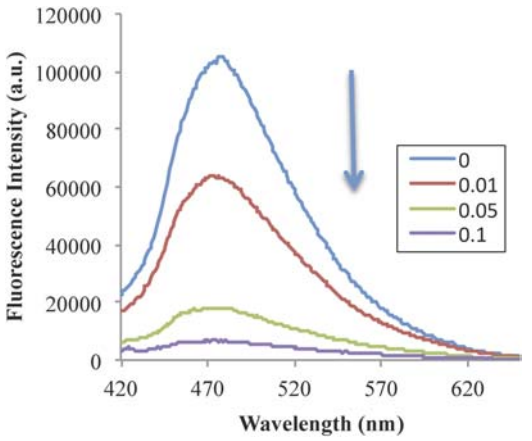


Figure 3. (Colour online) Fluorescence quenching of **Zn-Cav** by NT in acetonitrile. NT concentrations from the top spectrum to the bottom were 0, 0.010, 0.050 and 0.10 M.

The Stern–Volmer constant for DMNB was much lower and was 4.3 M^{-1}. The nitro compounds were also titrated with **6** and Stern–Volmer constants were calculated. The constants were similar to those for **Zn-Cav** and were 108 M^{-1} (4-NT), 203 M^{-1} (2,4-DNT) and 3.2 M^{-1} (DMNB). The binding constants of the free arm are similar to those of the cavitand, and thus the cavitand does not enhance fluorescence quenching. This is probably due to solvent, such as DMSO, occupying the cavity of **Zn-Cav**. These constants of **Zn-Cav** are comparable to those of other Zn-salen compounds (*10*). The fluorescence quenching is a dynamic process, which most likely involves the nitro compounds bombarding with the Zn-salen moieties, resulting in energy transfer.

Conclusion

A resorcinarene-based cavitand containing a Zn-salen group has been synthesised and characterised. Along with the Zn-salen functional group, the cavitand has three quinoxalines. In organic solvents, such as DMSO, acetone and chloroform, the cavitand is in the vase conformation, but its conformation changes to the kite under acidic conditions. Due to the Zn-salen arm, the cavitand absorbs visible light and fluoresces. The fluorescence of the cavitand is quenched by 4-NT, 2,4-DNT and DMNB and thus could be beneficial to detect nitro-containing compounds.

Experimental

General

All reagents were used directly as supplied. 2,3-Dichloroquinoxaline (*7*) and the methyl-footed resorcinarene (*2*) were prepared following the literature procedures. NMR spectra were obtained from a Varian 300 or 500 MHz instrument. Mass spectra were taken on an Agilent TOF ESI MS instrument in positive mode unless otherwise stated. Absorbance measurements were taken on a Hewlett Packard 8453 spectrophotometer. Steady-state luminescence measurements were taken using a quartz cuvette with a Photon Technology International (PTI) Bryte Box fluorometer.

6-Nitro-2,3-dihydroxyquinoxaline (2)

To 30 ml 1:1 H_2O/HCl was added 4-nitro-o-phenylenediamine (7.480 g, 0.048 mol) and oxalic acid (6.602 g, 0.073 mol). The solution was stirred 21 h under reflux at 115°C. A grey precipitate formed which then was filtered and washed in 2 × 10 ml H_2O, 2 × 10 ml ethanol and 2 × 10 ml ether. The precipitate was dried under vacuum and weighed 10.67 g (94%). ^{1}H NMR (300 MHz, DMSO-d_6, 25°C): δ 12.36 (1H, s, OH), 12.16 (1H, s, OH), 7.97 (2H, m, ArH), 7.24 (1H, d, $J = 8.5$, ArH) ppm. ^{13}C NMR (500 MHz, DMSO-d_6, 25°C): δ 155.6, 155.1, 142.5, 132.1, 126.5, 119.0, 115.9, 110.7 ppm. HRMS (ESI negative): *m/z* calcd for $C_8H_5N_3O_4 - H^+$: 206.03; found 206.04.

6,7-Dinitro-2,3-dihydroxyquinoxaline (3)

KNO_3 (10.67 g, 0.051 mol) was dissolved in 45 ml of concentrated H_2SO_4 and 6-nitro-2,3-dihydroxyquinoxaline (10.15 g, 0.049 mol) was slowly added to it at 0°C while stirring. The solid dissolved and the solution was stirred for 1 h. The reaction was then brought to room temperature and allowed to stir for 18 h. The reaction solution was then poured into 100 ml of stirred ice water and a yellow precipitate formed. The precipitate was filtered and washed 2 × 20 ml H_2O, 2 × 20 ml ethanol and 2 × 20 ml ether. The solid was dried under vacuum and weighed 9.89 g (76 %). ^{1}H NMR (300 MHz, DMSO-d_6, 25°C): δ 12.50 (2H, s, OH), 7.72 (2H, s, ArH) ppm. ^{13}C NMR (500 MHz, DMSO-d_6, 25°C): δ 155.2, 137.4, 130.0, 112.2 ppm. HRMS (ESI negative): *m/z* calcd for $C_8H_4N_4O_6 - H^+$: 251.01; found 251.02.

2,3-Dichloro-6,7-dinitroquinoxaline (4)

2,3-Dihydroxy-6,7-dinitroquinoxaline (6.80 g, 0.027 mol) and 3.0 ml of N,N-dimethylaniline were added to 18 ml $POCl_3$ and the mixture was brought to reflux at 110°C for 18 h. The red solution was cooled and poured into 150 ml of stirred ice water, upon which a red precipitate formed. The precipitate was filtered, washed with 5 × 30 ml of water and dried under vacuum. The precipitate was then extracted eight times in 100 ml of benzene, and the benzene solution was filtered and evaporated to a red crystalline solid (5.18 g, 66.4%). ^{1}H NMR (300 MHz,

DMSO-d_6, 25°C): δ 9.08 (2H, s, ArH) ppm. ^{13}C NMR (500 MHz, DMSO-d_6, 25°C): δ 151.4, 143.5, 140.9, 126.3 ppm. HRMS (ESI, ethyl acetate): *m/z* calcd for $C_8H_2Cl_2N_4O_4{\cdot}C_4H_8O_2$: 376.00; found 376.34.

2,3-Dichloro-6,7-diaminoquinoxaline (5)

2,3-Dichloro-6,7-dinitroquinoxaline (2.6 g, 0.0090 mol) and $SnCl_2{\cdot}2H_2O$ (12.56 g, 0.054 mol) were dissolved in 60 ml ethanol and stirred for 30 min, after which 120 drops of HCl were added from a Pasteur pipet. After the reaction mixture was stirred for 18 h, it was evaporated until no more solvent could be pulled off (about 1/10 of total solution remained) and poured into 50 ml ice water. The brown precipitate that was formed was filtered, washed in 6 × 30 ml water and air-dried. It was then extracted with methanol until no more solid dissolved and the methanol solution evaporated to dryness to yield 1.44 g (70.0 %). ^{1}H NMR (300 MHz, DMSO-d_6, 25°C): δ 6.81 (2H, s, ArH), 6.13 (4H, s, NH) ppm. ^{13}C NMR (500 MHz, DMSO-d_6, 25°C): δ 143.5, 138.1, 137.4, 104.0 ppm. HRMS (ESI negative): *m/z* calcd for $C_8H_6Cl_2N_4 - H^+$: 227.00; found 227.01.

Zn-salen complex (6)

Compound **6** was synthesised by a procedure similar to related compounds (*14*). 2-Hydroxy-3-methylbenzaldehyde (0.365 ml, 3.2 mmol) and $Zn(OAc)_2{\cdot}2H_2O$ (0.358 g, 1.6 mmol) were added to methanol (40 ml) and the mixture was stirred for 30 min at room temperature. Then 2,3-dichloro-6,7-diaminoquinoxaline (0.366 g, 1.6 mmol) was added to the solution. The solution was stirred for 28 h and the resulting deep orange precipitate was collected by filtration, washed 3 × 20 ml with ice-cold methanol and dried under vacuum. Yield: 0.430 g (50.8%). ^{1}H NMR (300 MHz, DMSO-d_6, 25°C): δ 9.20 (2H, s, NCH), 8.48 (2H, s, ArH), 7.34 (2H, m, ArH), 7.26 (2H, m, ArH), 6.46 (2H, m, ArH), 2.20 (6H, s, CH_3) ppm. ^{13}C NMR (500 MHz, DMSO-d_6, 25°C): δ 172.6, 166.4, 144.5, 144.0, 139.9, 135.4, 135.0, 131.1, 118.8, 113.7, 113.4, 17.3 ppm. HRMS (ESI): *m/z* calcd for $C_{24}H_{16}N_4O_2Zn + H^+$: 528.99; found 529.00.

Preparation of resorcinarene with 3 quinoxalines (7)

Resorcinarenes with different numbers of quinoxalines were obtained by using procedures reported in the literature and the resorcinarene containing three quinoxalines was isolated from the mixture (*12*). To a solution of resorcinarene-based methyl bowl (1.65 g, 3.01 mmol) in dry DMSO (40 ml), K_2CO_3 (0.416 g, 3.01 mmol) and 2,3-dichloroquinoxaline (1.20 g, 6.02 mmol) were added and the mixture was stirred for 1 h under N_2. More K_2CO_3 (0,832 g, 6.02 mmol) was added and stirring under N_2 was continued for 18 h at room temperature and for 6 h at 50°C. After cooling, the brown solution was added to H_2O (50 ml) and the pH was adjusted to 6–7 by addition of 1 M HCl. The pink precipitate that formed was isolated by filtration, washed with H_2O (50 ml) and dried under vacuum. Column chromatograph (200 g of SiO_2 in 250 ml capacity column flask; CH_2Cl_2/AcOEt 95:5 → 85:5) afforded resorcinarenes with four quinoxalines (827 mg), three quinoxalines (133 mg) and two quinoxalines (191 mg). The mass spectrum and ^{1}H NMR spectra matched the reported values for the resorcinarene with three quinoxalines: R_f (SiO_2; CH_2Cl_2/AcOEt 90:10): 0.15. ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ 1.81–1.82 (3H, m), 1.92–1.93 (6H, m), 2.00–2.04 (3H, m), 4.51–4.53 (4H, m), 4.51–4.53 (1H, m), 5.60–5.61 (2H, m), 5.75 (1H, m), 6.960 (2H, m), 7.64–47.67 (2H, m), 7.75–7.77 (4H, m), 7.81–7.83 (2H, m), 8.02–8.03 (2H, m), 8.09–8.11 (2H, m), 8.11 (2H, s), 9.82 (2H, s) ppm. HRMS (ESI): *m/z* calcd for $C_{56}H_{38}N_6O_8 + H^+$: 923.28; found 923.29.

Synthesis of Zn-Cav

To resorcinarene **7** (0.067 g, 0.067 mmol) and **6** (0.036 g, 0.067 mmol) in dry DMSO (2.5 ml), K_2CO_3 (0.012 g, 0.084 mmol) was added and the mixture stirred under N_2 at 50°C for 48 h. After addition of H_2O to the mixture, an orange precipitate formed, which was isolated by filtration, washed with H_2O and dried under vacuum to yield 0.048 g (52%). ^{1}H NMR (500 MHz, DMSO-d_6, 25°C): δ 1.91–1.95 (12H, m, CH_3), 2.27 (6H, s, CH_3), 5.70 (4H, m, CH), 6.50 (2H, m, $Ar_{salen}H$), 6.94 (2H, m, $Ar_{quin}H$), 7.28 (2H, m, $Ar_{salen}H$), 7.40 (2H, m, $Ar_{salen}H$), 7.59 (2H, m, $Ar_{quin}H$), 7.60 (2H, m, $Ar_{quin}H$), 7.79–7.81 (2H, m, $Ar_{quin}H$), 7.87–7.88 (2H, m, $Ar_{quin}H$), 7.95 (4H, s, $Ar_{res}H$), 8.02 (2H, s, $Ar_{res}H$), 8.09 (2H, s, $Ar_{res}H$), 8.15–8.16 (2H, m, $Ar_{quin}H$), 8.41 (2H, s, $Ar_{salen}H$), 9.54 (2H, s, NCH). ^{13}C NMR (500 MHz, DMSO-d_6, 25°C): δ 172.4, 165.2, 152.3, 152.1, 151.7, 142.4, 139.5, 139.4, 138.7, 137.4, 135.4, 134.8, 131.1, 129.9, 129.3, 128.0, 127.8, 125.5, 119.0, 118.3, 113.4, 28.9, 18.9, 18.7, 17.3 ppm. HRMS (ESI): *m/z* calcd for $C_{80}H_{52}N_{10}O_{10}Zn{\cdot}8H_2O + H^+$: 1521.40; found 1521.95. Elemental analysis calcd (%) for $C_{80}H_{52}N_{10}O_{10}Zn{\cdot}C_2H_6OS{\cdot}7H_2O$ 1582.95: C 62.22, H 4.58, N 8.85; found C 62.00, H 4.66, N 8.66. (Water and DMSO were verified by ^{1}H NMR.)

Fluorescence quenching

Absorbance and fluorescence measurements were collected in a 1 cm path length quartz cuvette in DMSO, chloroform and acetonitrile. Quinine sulfate in 0.1 M H_2SO_4 was used as a standard and exited at 400 nm and the emission monitored at 450 nm (Ø = 0.54) (*15*, *16*). Solutions of **Zn-Cav** and **6** were also excited at 400 nm

and monitored at $\lambda_{em} = 470–480$ nm. The resulting fluorescence intensities were plotted against solution absorbance to generate a linear plot to calculate the quantum yield of the compound in different solvent environments. Analysis of the normalised fluorescence intensity (I_o/I) as a function of increasing quencher concentration ([Q]) was well described by the Stern–Volmer equation, $I_o/I = 1 + K_{sv}[Q]$, for all titrations.

Supporting Information Available

NMR spectra and Stern–Volmer plots are available via the Internet.

Acknowledgement

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