

Supplementary Information for
Encapsulating Zinc(II) Within a Hydrophobic Cavity

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Experimental Section

General Considerations. Unless otherwise stated, all operations were performed in a VAC Atmosphere double-dry box under an atmosphere of purified nitrogen or using high vacuum standard Schlenk techniques under a nitrogen atmosphere. Anhydrous *n*-hexane, pentane, toluene, tetrahydrofuran, diethyl ether, acetonitrile and benzene were purchased from Aldrich and dried with a SG Waters solvent purification system. Dimethoxyethane (DME) was dried over lithium aluminum hydride overnight, distilled and dried further with 4 Å activated alumina, filtered through a bed of activated alumina powder, and stored over 4 Å molecular sieves. Anhydrous dimethylformamide (DMF) was purchased from Aldrich and further dried using 4 Å activated alumina, filtered through a bed of activated alumina powder and stored over 4 Å molecular sieves. CDCl₃ and *d*₆-DMSO were purchased from Cambridge Isotope Laboratory (CIL), degassed and stored over 4 Å molecular

sieves. Celite, alumina, and 4 Å molecular sieves were activated under vacuum for four days at 350°C. 1,3,5-tri(3-butenyl)benzene (**1**) was prepared according to modified literature procedures.¹ All other chemicals were used as received. ¹H and ¹³C NMR data/spectra were recorded on Varian 300 and 500 MHz NMR spectrometers. ¹H and ¹³C NMR are reported with reference to solvent resonances.

Synthesis and Characterization

1,3,5-tris((9-borabicyclo[3.3.1]nonan-9-yl)butyl)benzene (2): Inside the glovebox, 1,3,5-tri(3-butenyl)benzene (10.2 g, 42.3 mmol) was dissolved in 300 mL of THF, and a solution of 9-borabicyclo[3.3.1]-nonane dimer (9-BBN) (15.5 g, 63.4 mmol) was added portion-wise at room temperature. The mixture was stirred for 12 hours and the solvent was removed to yield 24.4 g (95% yield) of thick yellow oil. For **2**: ¹H NMR (23 °C, 300 MHz, CDCl₃): δ 6.83 (s, 3H, C₆H₃), 2.58 (t, 6H, (C₆H₃)CH₂CH₂CH₂CH₂B), 1.84 (m, BBN), 1.69 (m, BBN), 1.56 (m, (C₆H₃)CH₂CH₂CH₂CH₂B), 1.39 (m, (C₆H₃)CH₂CH₂CH₂CH₂B), 1.20 (m, BBN). ¹³C NMR (23 °C, 75 MHz, CDCl₃): δ 142.53 (C₆H₃), 125.37 (C₆H₃), 35.76 (BCHCH₂CH₂), 34.65 ((C₆H₃)CH₂CH₂CH₂CH₂B), 33.2 ((C₆H₃)CH₂CH₂CH₂CH₂B), 32.91 (BCHCH₂CH₂), 30.76 ((C₆H₃)CH₂CH₂CH₂CH₂B), 23.98 ((C₆H₃)CH₂CH₂CH₂CH₂B), 23.02 (BCHCH₂CH₂).

¹ J. K. Twibanire, H. Al-Mughaid, T. B. Grindley *Tetrahedron*, 2010, **66**, 9602.

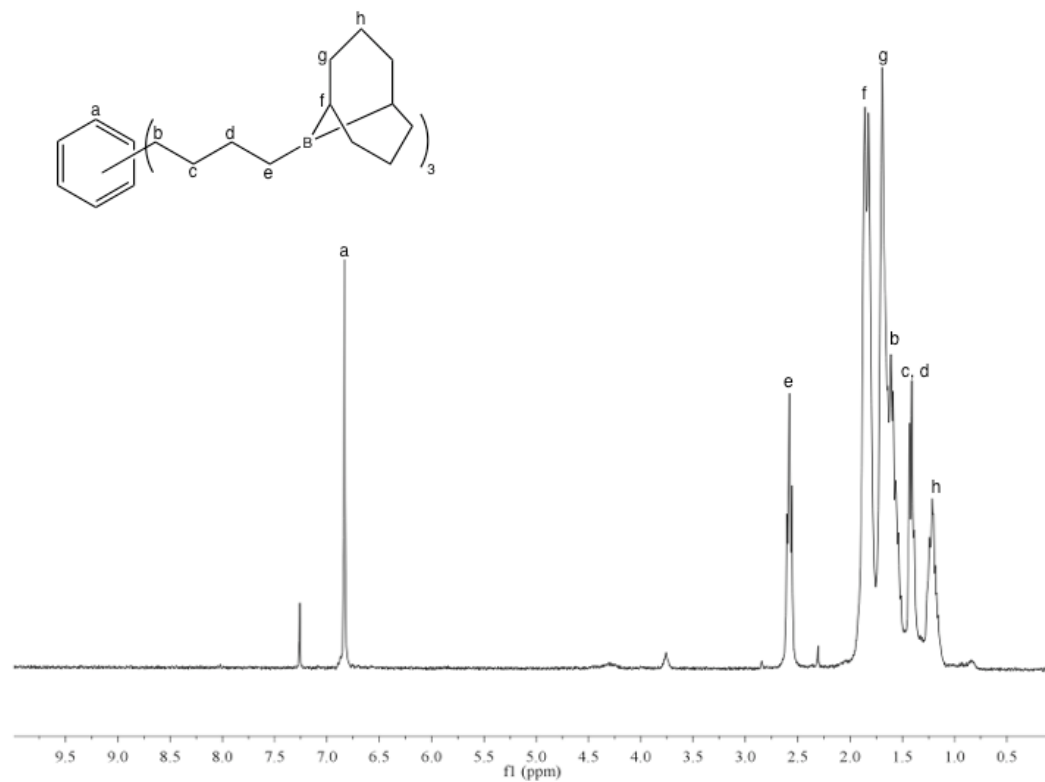


Figure S1. ¹H NMR spectrum of **2** (23 °C, 300 MHz, CDCl₃).

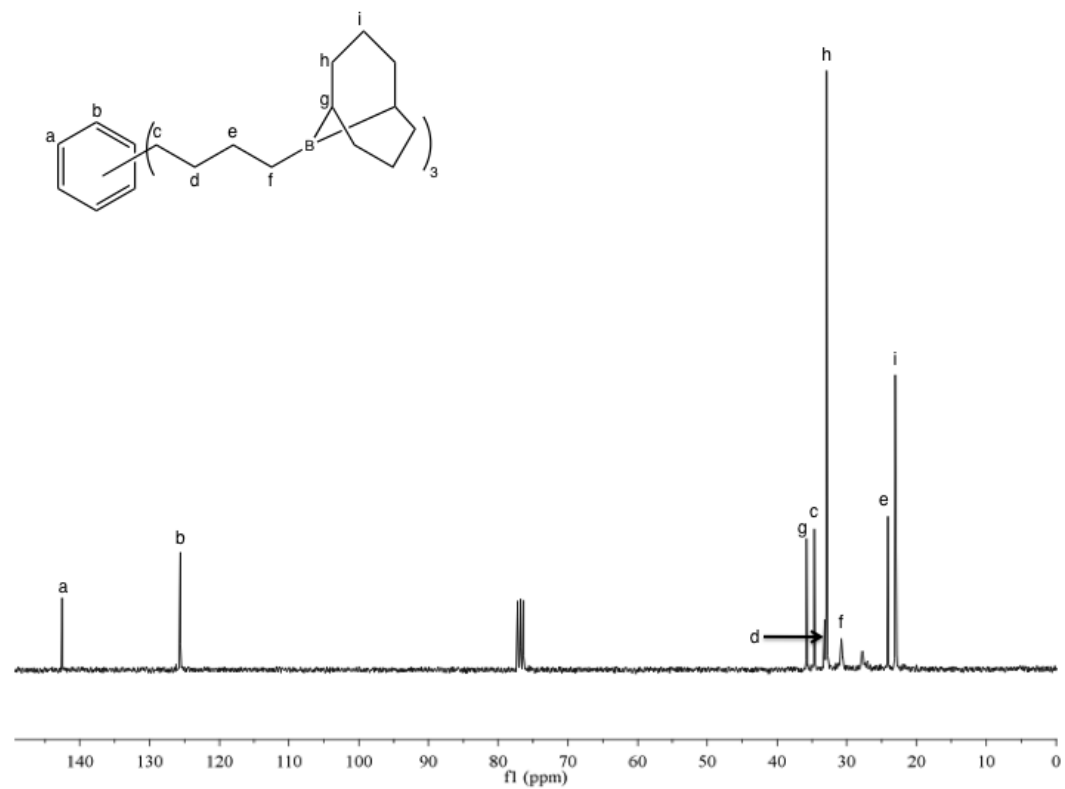


Figure S2. ¹³C NMR spectrum of **2** (23 °C, 75 MHz, CDCl₃).

Tris 1,3,5-(butyl-4-benzoate) benzene (3): A bomb flask was charged with **2** (3.29 g, 543 mmol), 4-methyl iodobenzoate (7.12 g, 27.0 mmol), K₂CO₃ (11.25 g, 81.0 mmol), PdCl₂(dppf)CH₂Cl₂ (664 mg, 15 mol%), and 250 mL of DMF. The reaction was heated in a 50 °C oil bath for 36 hours, after which the DMF was removed via vacuum distillation. The resulting maroon residue was extracted into CH₂Cl₂. After the solvent was removed, the dark red residue was redissolved in minimal amounts of CH₂Cl₂ and filtered through a pad of celite. The resulting oil was purified on a short silica plug with a 10 % EtOAc/Hexane eluting mixture. The orange oil was further purified by column chromatography (silica, gradient (5-10 % EtOAc/Hexane) to yield 2.05 g (59 %) of pure colorless oil. For **3**: ¹H NMR (23 °C, 500 MHz, CDCl₃): δ 7.95 (d, 6H, (C₆H₄)COCH₃), 7.23 (d, 6H, (C₆H₄)COCH₃), 6.77 (s, 3H, (C₆H₃)(CH₂)₄), 3.87 (s, 3H, (C₆H₄)COCH₃), 2.67 (t, 6H, (C₆H₃)(CH₂)₄), 2.56 (t, 6H, (C₆H₃)(CH₂)₄), 1.66 (m, 12H, (C₆H₃)(CH₂)₄). ¹³C NMR (23 °C, 75 MHz, CDCl₃): δ 147.9 (COOMe), 142.0 (C₆H₃), 129.4 (C₆H₄), 128.2 (C₆H₄), 127.4 (C₆H₄), 125.7 (C₆H₃), 105.2(C₆H₄), 51.8 (COOMe), 35.6 (CH₂CH₂CH₂CH₂), 35.4 (CH₂CH₂CH₂CH₂), 30.8 (CH₂CH₂CH₂CH₂), 30.6 (CH₂CH₂CH₂CH₂).

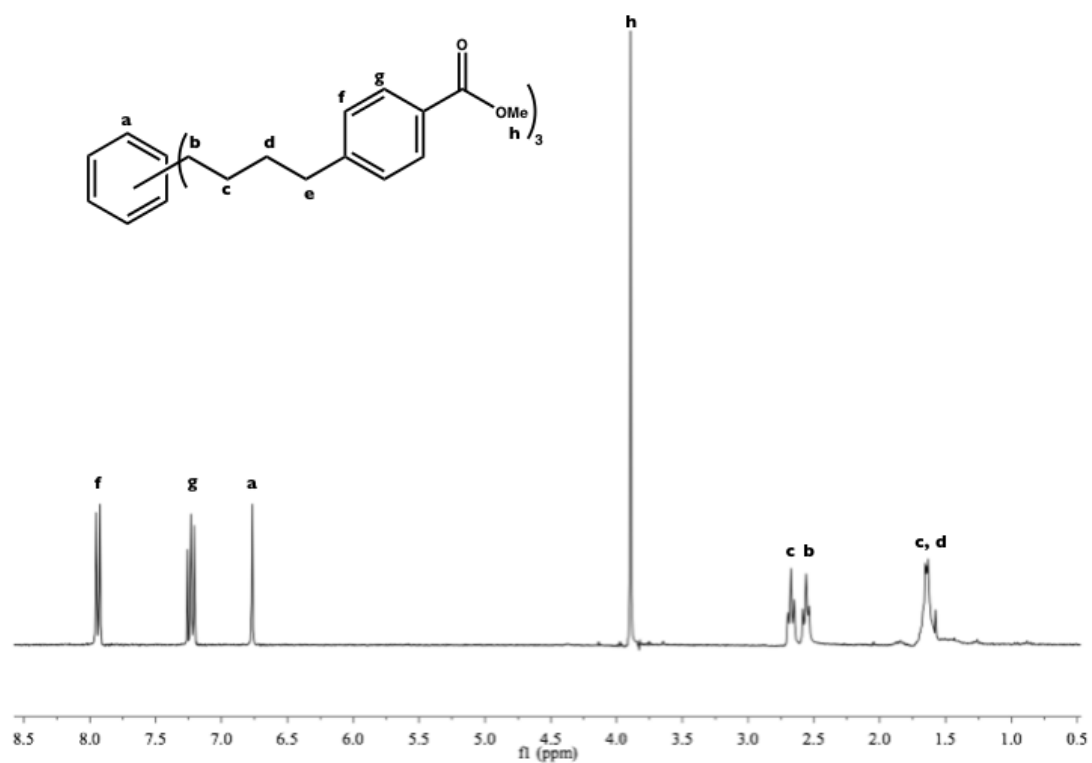


Figure S3. ¹H NMR spectrum of **3** (23 °C, 500 MHz).

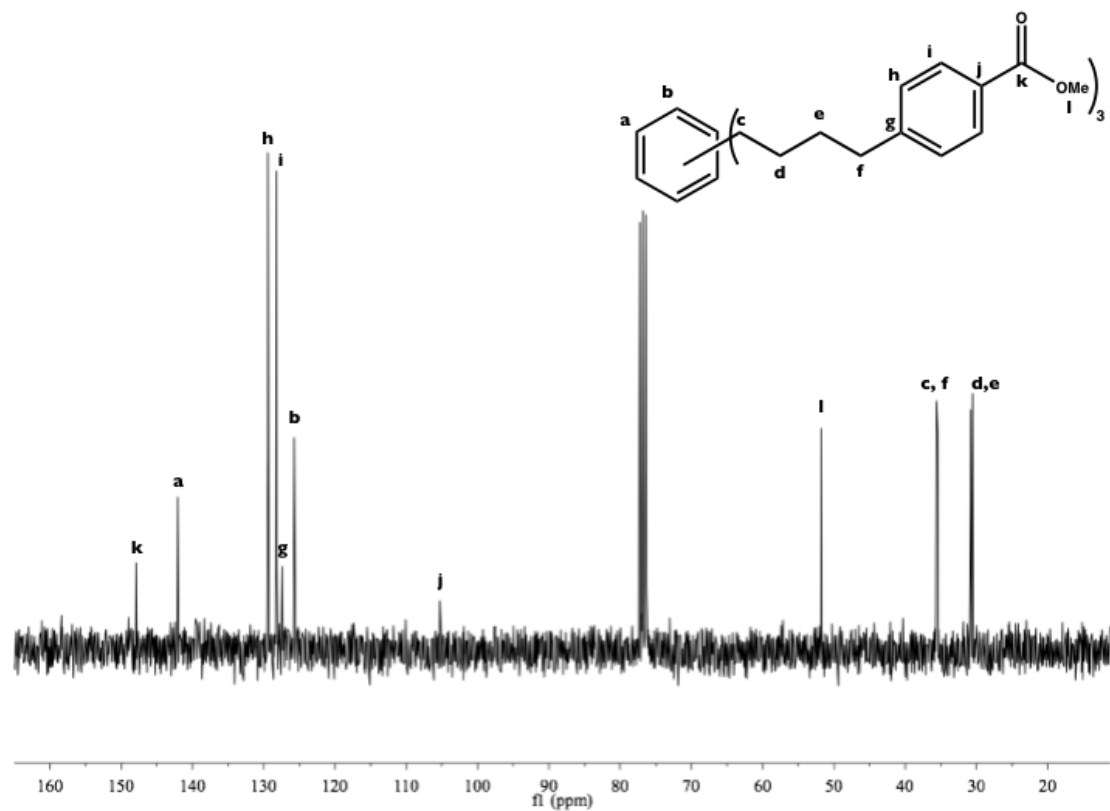


Figure S4. ¹³C NMR spectrum of **3** (23 °C, 75 MHz, CDCl₃).

Tris 1,3,5-(butyl-4-benzoic acid) benzene (4): A round bottom was charged with **2** (4.0 g, 6.2 mmol) dissolved in a mixture of MeOH and H₂O (10:1). 250 mL of a 5M KOH solution was added to the stirring solution. After 24 hrs of stirring a white precipitate had formed and the reaction was quenched with 250 mL of a 6M HCl solution. The product was extracted into Et₂O (3 x 100 mL) and isolated as a white solid (3.3 g) in an 87 % yield. For **3**: ¹H NMR (23 °C, 500 MHz, *d*₆-DMSO): δ 12.77 (br s, 3H, COOH), 7.83 (d, 6H, C₆H₄), 7.27 (d, 6H, C₆H₄), 6.75 (s, 3H, C₆H₃), 2.63 (t, 6H, (CH₂)₄), 2.51 (t, 6H, (CH₂)₄), 1.54 (m, 12H, (CH₂)₄). ¹³C NMR (23 °C, 75 MHz, *d*₆-DMSO): δ 167.79 (COOH), 148.13 (C₆H₃), 142.30 (C₆H₄), 129.85 (C₆H₄), 128.12 (C₆H₄), 128.77 (C₆H₄), 126.20 (C₆H₃), 35.30 ((C₆H₃)CH₂CH₂CH₂CH₂(C₆H₄)), 30.99 ((C₆H₃)CH₂CH₂CH₂CH₂(C₆H₄)), 30.66 (((C₆H₃)CH₂CH₂CH₂CH₂(C₆H₄)).

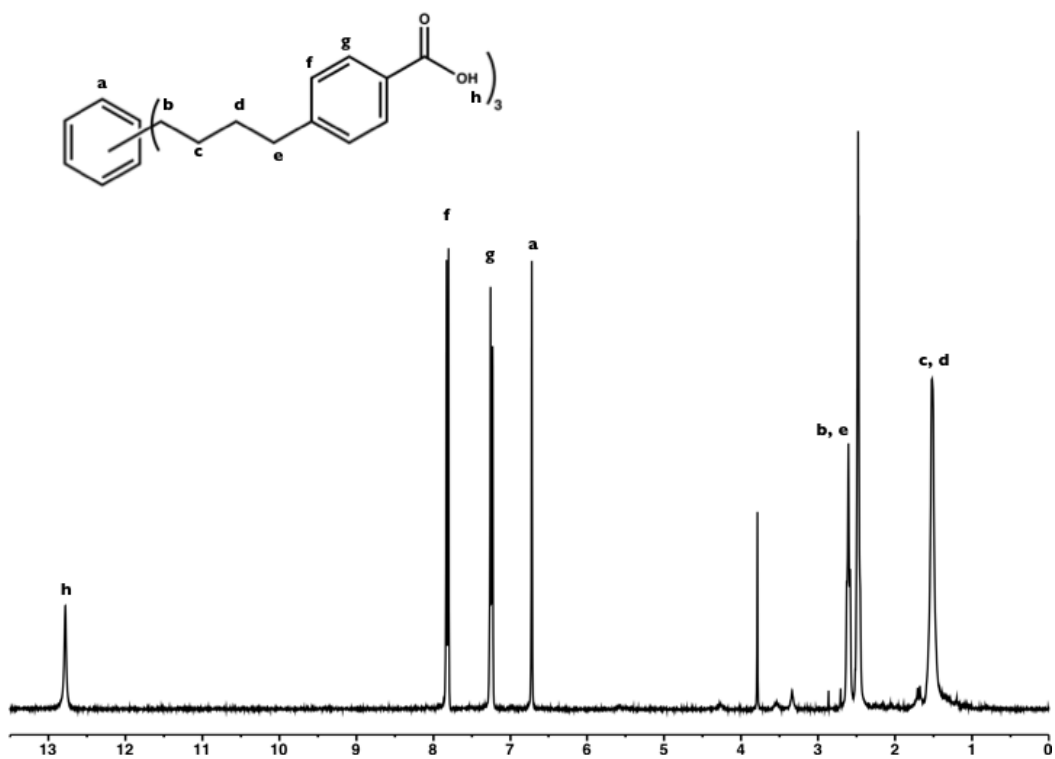


Figure S5. ¹H NMR spectrum of **4** (23 °C, 500 MHz, *d*₆-DMSO).

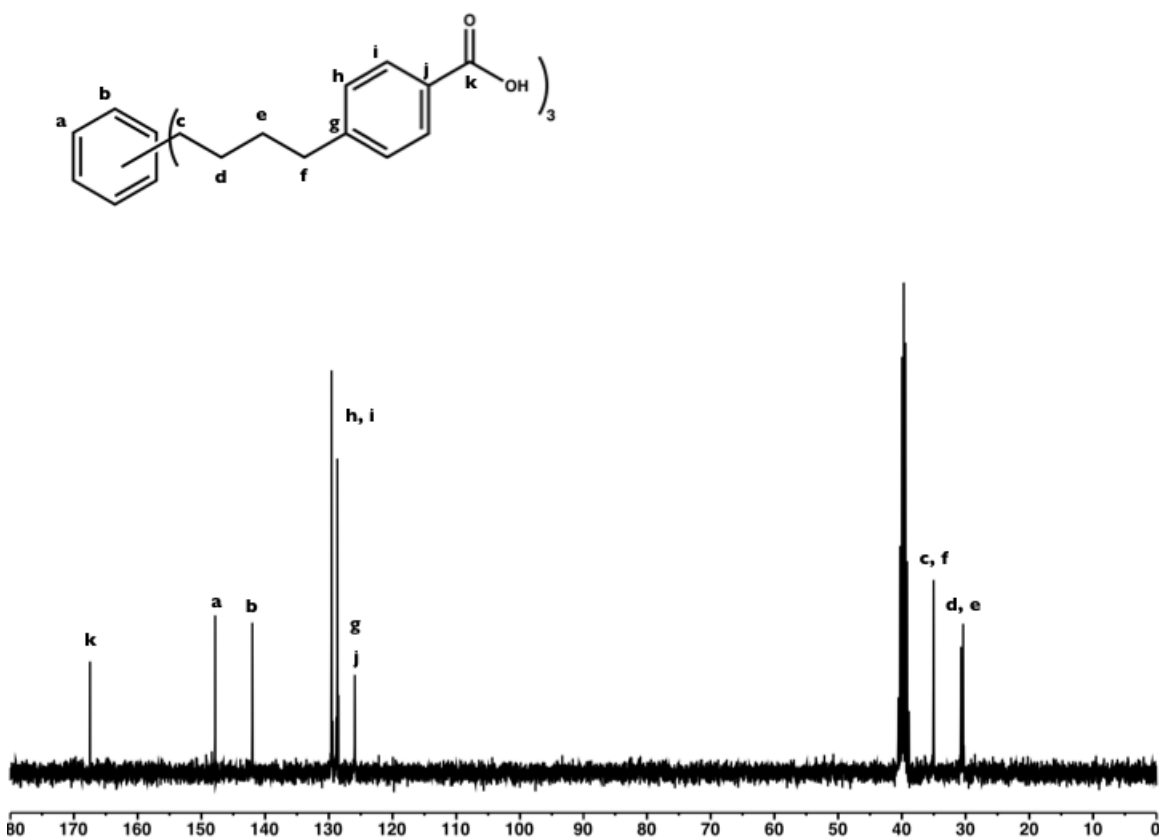


Figure S6. ^{13}C spectrum NMR of **4** (23 °C, 75 MHz, d_6 -DMSO).

Proligand (5): A round bottom was charged with **4** (1.05 g, 1.7 mmol) dissolved in THF and 1.18 g (5 mmol) of dipyridyl-disulfide was added as a THF solution. Solid PPh_3 (1.41 g, 5 mmol) was added and the reaction turned yellow immediately. After stirring at room temperature for 12 hrs, the solvent was removed. The residue was dissolved in 450 mL of toluene and fitted with a 500 mL addition funnel charged with 258.7 μL (1.7 mmol) of tris(2-aminoethyl)amine (tren) in 450 mL of toluene. The tren solution was added dropwise over 4 hours and the reaction was refluxed for 12 hrs. After 12 hrs of refluxing, some white solids had precipitated. They were filtered off and the solvent was removed to yield a yellow residue. Et_2O was added

and a white solid precipitate. The solid was collected to yield 0.766 g (64 %) of **5**.
For **5**: ^1H NMR (23 °C, 500 MHz, d_6 -DMSO): δ 7.70 (broad, t, 3H, NH), 7.26 (d, 6H, $(\text{CH}_2)_4(\text{C}_6\text{H}_4)\text{CH}_2\text{NH}$), 6.87 (s, 3H, C_6H_3), 6.74 (d, 6H, $(\text{CH}_2)_4(\text{C}_6\text{H}_4)\text{CH}_2\text{NH}$), 3.31 (broad, $\text{NHCH}_2\text{CH}_2\text{N}$), 2.61 (t, 6H, $\text{NHCH}_2\text{CH}_2\text{N}$), 2.54 (m, 6H, $(\text{CH}_2)_4$), 2.36 (m, 6H, $(\text{CH}_2)_4$), 1.70 (m, 6H, $(\text{CH}_2)_4$), 1.29 (m, 6H, $(\text{CH}_2)_4$). ^{13}C NMR (23 °C, 75 MHz, d_6 -DMSO): δ 166.72, 145.41, 140.93, 127.42, 126.95, 125.97, 53.53, 37.08, 35.07, 33.92, 29.06. ESI-TOF HRMS (MeOH) with PPG-500-800 m/z : $[\text{M} + \text{Na}]^+$ calculated for $\text{C}_{45}\text{H}_{54}\text{N}_4\text{NaO}_3$, 721.4094; found, 721.4087; 0.97 ppm error.

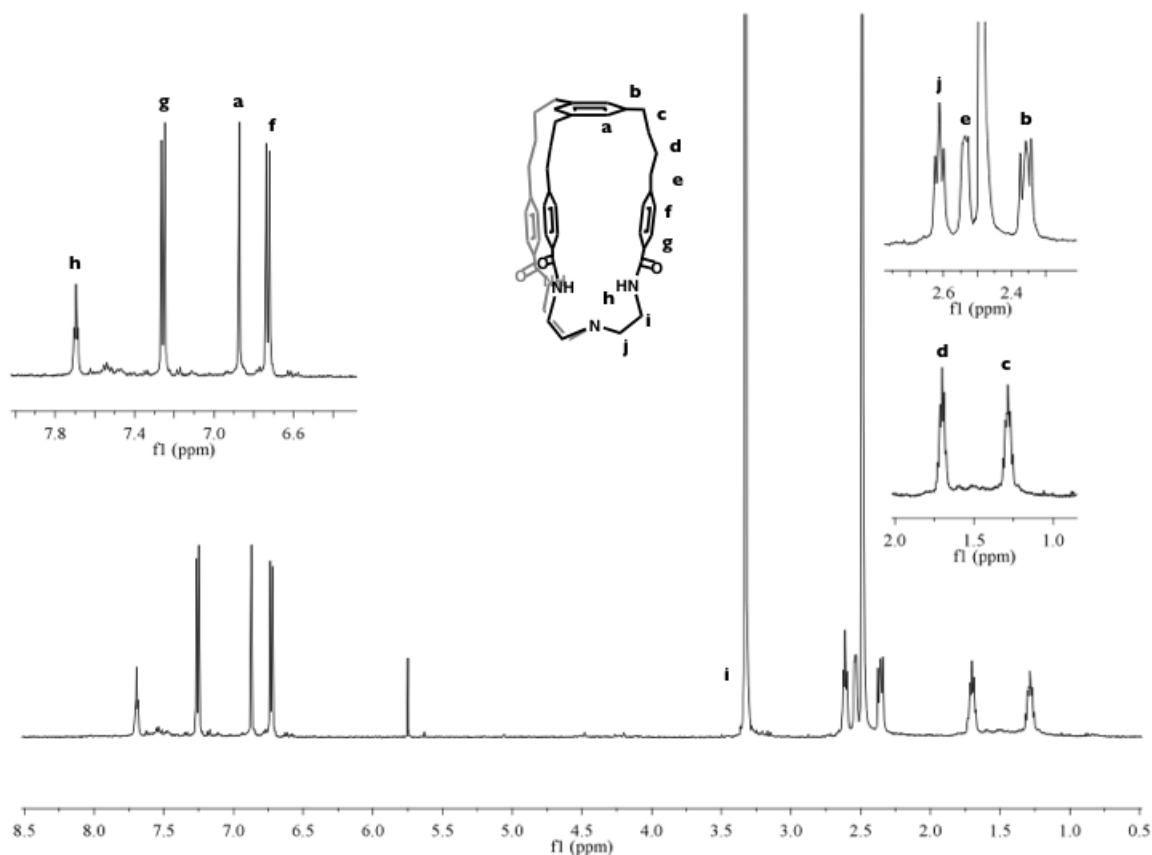


Figure S7. ^1H NMR spectrum of **5** (23 °C, 500 MHz, d_6 -DMSO).

Zn(II) complex (6): 5 (0.237 mmol) was dissolved in DMA and a solution of KH (0.949 mmol) was added slowly at room temperature to result in a dark red-brown solution. After 30 min of stirring, ZnCl₂ (0.237 mmol) was dissolved in DMA and added dropwise to the deprotonated ligand. An immediate color change to a light maroon color was observed. After stirring for 12 hrs, the reaction mixture was filtered through a pad of celite to remove the KCl. The resulting filtrate was stirred vigorously while copious amounts of Et₂O was added to crash out the potassium salt of **6**. The salt was isolated as a fluffy pink powder (173 mg) in a 91 % yield. For **[K(DMSO)_n][Zn(L)]**: ¹H NMR (23 °C, 500 MHz, *d*₆-DMSO): δ 7.13 (d, 6H, C₆H₄), 6.89 (s, 3H, C₆H₃), 6.37 (d, 6H, C₆H₄), 3.32 (t, 6H, NCH₂CH₂N), 2.64 (m, 6H, (CH₂)₄), 2.59 (t, 6H, NHCH₂CH₂N), 2.16 (m, 6H, (CH₂)₄), 1.77 (m, 6H, (CH₂)₄), 1.17 (m, 6H, (CH₂)₄). A crystal suitable for single crystal X-ray crystallography was obtained by exchanging the potassium cation with PPh₄ and isolating from a hot THF solution. Elemental Analysis was obtained using the same crystals **[PPh₄][Zn(L)] 6'**: Anal. Calcd for C₆₉H₇₁N₄O₃PZn: C, 75.29; H, 6.50; N, 5.09. Found: C, 74.93; H, 6.68; N, 5.26.

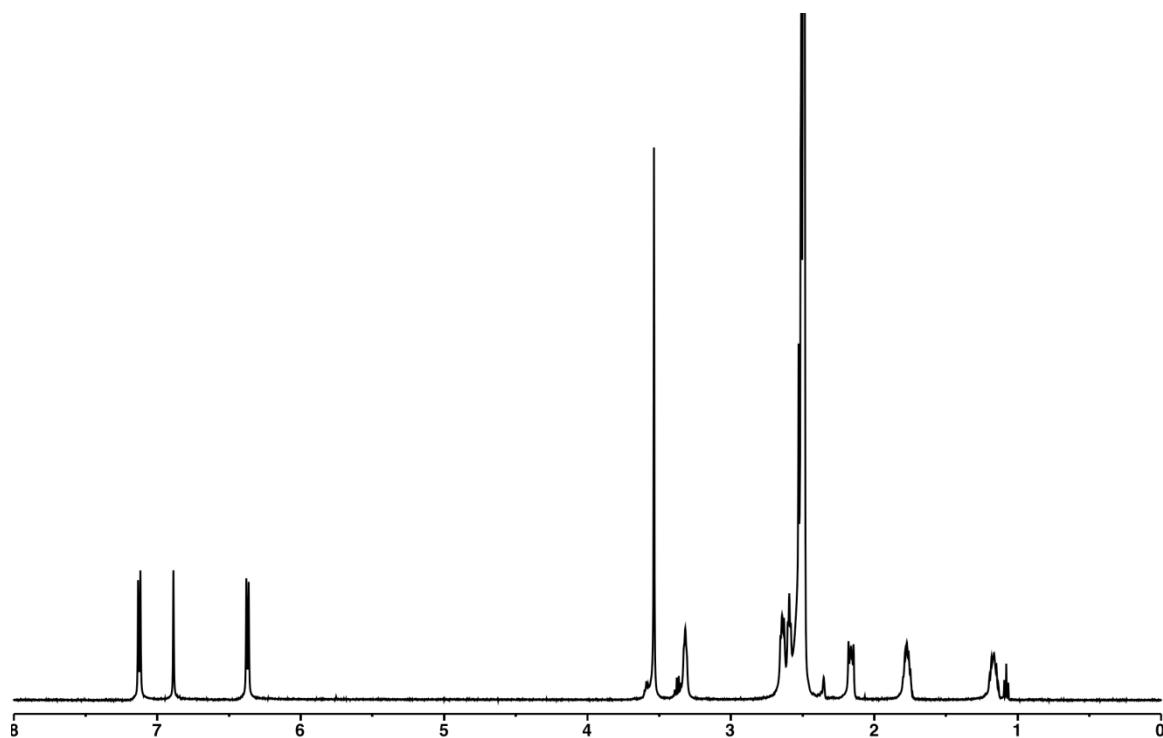


Figure S8. ^1H NMR spectrum of **6**[K(**18-crown-6**)] (23 °C, 500 MHz, d_6 -DMSO).

Reactivity Studies

In a J-Young NMR tube, 10 mg of **6'** was dissolved in d_6 -DMSO and a ^1H NMR spectrum was obtained on a 500 MHz instrument. Using a microliter syringe, 10 μL of the substrate (pentane, hexane, benzene, acetonitrile, and trifluorotoluene) was added to the J-young tube and the reaction was analyzed by ^1H NMR spectroscopy.

Theoretical Calculations

Geometry optimizations and single-point energy calculations were performed using Gaussian09² and the M06-L³ functional. For zinc, nitrogen and oxygen triple zeta quality basis sets with one set of polarization functions were used (def2-TZVP).⁴ Carbon and hydrogen atoms were described by smaller polarized split-valence def2-SV(P) basis sets.⁴ The cavity heights were determined by measuring the distance from a centroid in the apical benzene ring to the metal center.

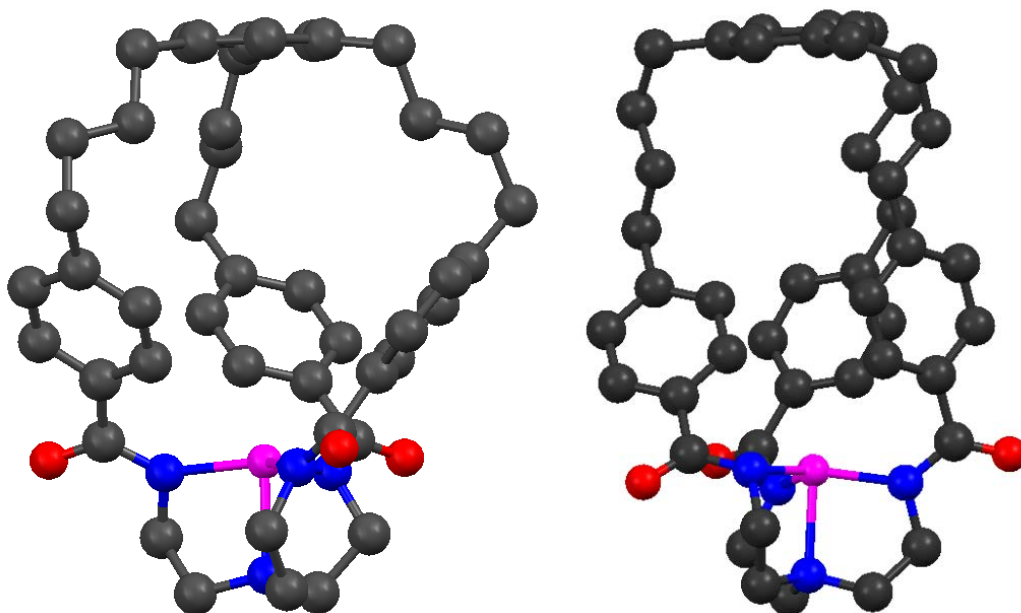


Figure S9. Geometry optimized structures of **6**. Left: initial coordinates were generated using Gaussian Viewer; Right: initial coordinates were taken from X-ray crystallographic coordinates.

² Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; J. A. Montgomery, J.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; N. Staroverov, V.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford, CT (2009).

³ (a) Zhao, Y.; Truhlar, D. G. *Acc. Chem. Res.* **2008**, *41*, 157-167. (b) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *125*, 194101-194118.

⁴ Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

X-Ray Crystallographic Data

Table 1. Crystallographic details for **6'**.

	6'
chemical formula	C ₇₃ H ₇₇ N ₄ O ₄ PZn
formula weight	1170.73
crystal system	monoclinic
space group	<i>P2₁/n</i>
<i>a</i> (Å)	13.1597(8)
<i>b</i> (Å)	34.881(2)
<i>c</i> (Å)	14.5029(9)
α (deg)	90
β (deg)	92.8190(10)
γ (deg)	90
<i>V</i> (Å ³)	6649.2(7)
<i>Z</i>	4
<i>D</i> _{calcd} (g cm ⁻³)	1.169
λ (Å), μ (mm ⁻¹)	0.71073, 0.443
<i>T</i> (K)	173(2)
θ range (deg)	1.66 to 26.65
reflns collected	13959
unique reflns	9502
data/restraint/parameters	13959 / 0 / 748
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>))	0.0523, 0.1247

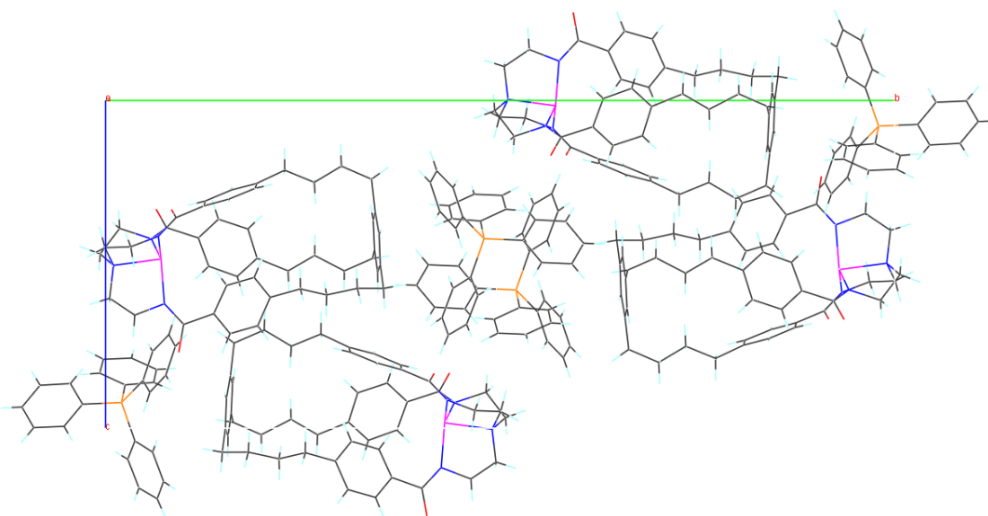


Figure S10. Depiction of the unit cell of **6'** looking down the *c*-axis.

PLATON⁵ Void Space Determination

The presence of long, open channels throughout the crystal lattice of an emissive transition metal complex can be advantageous for small-molecule sensing. Potentially, the empty cavities of **6'** could form a continuous channel in the crystal lattice. However, despite favorable alignment of the cavities along two unit cell vectors, a void space analysis revealed only short, disconnected channels, which are ill-suited for small-molecule transport (Figure S11 and S12).

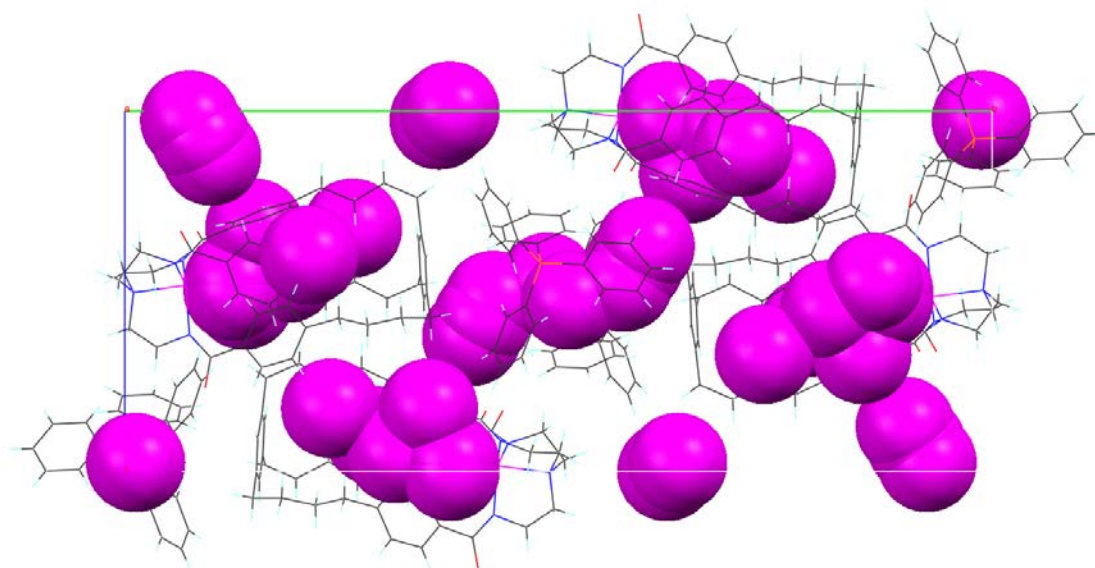


Figure S11. Depiction of void space (pink) determined by PLATON looking down the c-axis.

⁵ A.L.Spek, Acta Cryst. 2009, D65, 148-155.

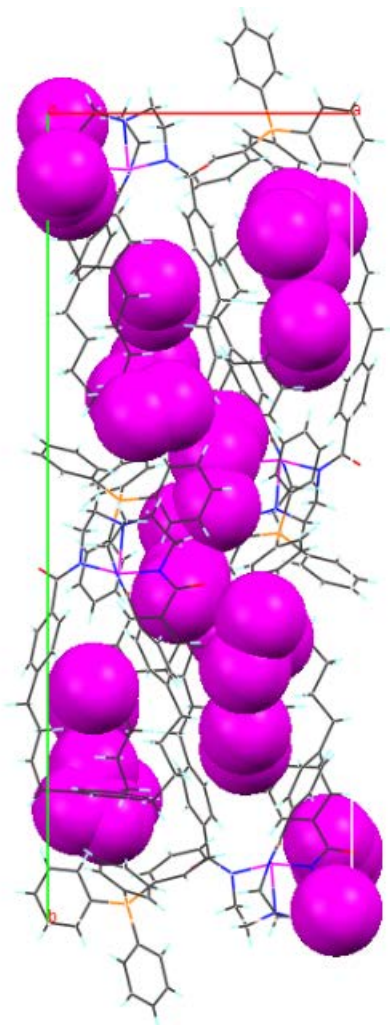


Figure S12. Depiction of void space (pink) determined by PLATON looking down the a-axis.