SUPPORTING INFORMATION

Synthesis, supramolecular complexation and DFTstudies of a bis(pyrene)appended "capped" triazole-linked calix[4]arene as Zn²⁺ and Cd²⁺ fluorescent chemosensors

Paris E. Georghiou,*¹ Shofiur Rahman,^{1,2}, Ahmad Alrawashdeh,¹ Abdullah Aloyhab,^{2,3} Gopikishore Valluru,¹ Kiran Sagar Unikela,¹ Graham J. Bodwell¹

¹ Memorial University of Newfoundland, Chemistry Dept., St. John's, Newfoundland and Labrador, Canada A1B3X7; ²Aramco Laboratory for Applied Sensing Research, King Abdullah Institute for Nanotechnology, KSU, Riyadh, Saudi Arabia. ³ Research Chair for Tribology, Surface, and Interface Sciences, Department of Physics and Astronomy, College of Science, King Saud University, Riyadh 11451, Saudi Arabia.

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Experimental section

The ¹H-NMR studies were conducted at 300 MHz using stock solution of **2g** (2.51×10^{-3} M) in CD₂Cl₂:CD₃CN (1:4, v/v) solvent with aliquots (1.98×10^{-1} M) of Cd(ClO₄)₂ or or Zn(ClO₄)₂ in the same solvent. UV-vis spectra in 1.0-cm sealed quartz fluorescence cuvettes were recorded on an Agilent 8543 Diode Array Spectrophotometer equipped with a continuous xenon arc lamp as the excitation source and interfaced to an HP computer. Data manipulations were conducted using software supplied by the manufacturer. Fluorescence emission spectra were measured on a Photon Technology International (PTI) Quanta Master 6000 spectrofluorometer equipped with a continuous xenon arc lamp as the excitation source. Apparent binding or association constants (K_{assoc}) using stock solutions of **2g** (2.02×10^{-5} M) in CH₃CN/CHCl₃ (9:1, v/v) were determined from titration studies with each of the metal ions as their perchlorate salts in the same mixed solvent and were based on the fluorescence data and calculated using Thordarson's non-linear global analytical software.¹ Stock solutions of the metal salts were prepared in (1.51 ×10⁻² M) in a CH₃CN:CHCl₃ (9:1) solvent mixture. DFT computations were conducted with Gaussian 09^2 and are described in the main text

2,10-Bis[6-(azidomethyl)pyren-2-yl]-2,10-dimethylundecane (**5**). A mixture of 2,10- bis(6-(bromomethyl)pyren-2-yl)-2,10-dimethylundecane³(**1**) (0.31 g, 0.42 mmol) and sodium azide (0.65 g, 4.0 mmol) was prepared in 15 mL of anhydrous DMF. The resulting solution was stirred for 24 h at room temperature. After completion of the reaction, saturated brine solution (25 mL) was added to the reaction mixture. The precipitated solid was filtered off and washed with water (20 mL) to yield **5** (in agreement with that previously reported²) as a yellow solid (0.21 g, 70%, m.p. 138.9-140.2 °C). ¹H-NMR (300 MHz, CDCl3) δ 8.22 (d, 2H, *J* = 9.3 Hz), 8.14–8.10 (m, 8H), 8.02 (d, 4H, *J* = 10.8 Hz), 7.92 (d, 2H, *J* = 7.5 Hz), 5.01 (s, 4H), 1.78–1.73 (m, 4H), 1.50 (s, 12H), 1.06–1.00 (m, 10H); ¹³C-NMR (CDCl3, 75.4 MHz): δ 148.1, 131.6, 130.9, 130.5, 129.0, 128.6, 128.1, 128.0, 127.1, 127.0, 124.9, 124.4, 123.5, 123.3, 122.8, 122.5, 53.1, 45.1, 38.2, 30.2, 29.5, 24.7; APCI(+) MS (*m*/*z*): 624.3 [M–N5]⁺.

5,11,17,23-Tetra-*tert***-butyl-25,27-dihydroxy-26,28-dipropargylcalix**[4]**arene** (6). A mixture of 1^4 (0.51 g, 0.78 mmol) and K₂CO₃ (0.24 g, 1.6 mmol) was heated at reflux for 1 h in acetone (30 mL). 3Propargyl bromide (0.19 g, 1.6 mmol) was added to the reaction mixture and then heated at reflux for 24 h. After cooling to room temperature, the reaction mixture was

neutralized with aqueous 1.0 M HCl and then extracted with ethyl acetate (3 × 50 mL), washed with water (2 × 50 mL). The separated organic layer was dried over anhydrous MgSO4 and the solvent was removed using a rotary evaporator. The residue was subjected to column chromatography (silica gel, 75:25 hexanes: ethyl acetate) to yield **6** (in agreement with that previously reported³) as a colourless solid (0.401 g, 71%, m.p. 222.0-223.3 °C): ¹H-NMR (CDCl3, 300 MHz): δ 7.07 (s, 4H, ArH), 6.72 (s, 4H, ArH), 6.50 (s, 2H, Ar-OH), 4.74 (d, 4H, J = 2.4 Hz, , –OCH2), 4.37 (d, 4H, Ar–CH2, J = 13.2 Hz), 3.33 (d, 4H, Ar–CH2, J = 13.2 Hz), 2.53 (t, 2H , , –C \Box CH, J = 2.4 Hz), 1.30 (s, 18H, *t*-Bu), 0.89 (s, 18H, *t*-Bu). ¹³C-NMR (CDCl3, 75.4 MHz): δ 150.4, 149.5, 147.2, 141.6, 132.6, 128.0, 125.5, 125.0, 78.8, 63.3, 33.9, 33.8, 32.0, 31.7, 30.9. APCI(+) MS (m/z): 725.4 [M+1]⁺.

5,11,17,23-Tetra-tert-butyl-25,27-dihydroxy-26,28-bis[1,2,3-triazol-1-methyl(2,10-bis-(6pyren-2-yl)-2,10-dimethylundecane)]calix[4]arene (2g). Copper iodide (0.041 g, 0.21 mmol) was added to a mixture of **6** (0.15 g, 0.21 mmol), diisopropylamine (20 μ L) and **5** (0.14 g, 0.21 mmol) in 20 mL of THF/H₂O (2:1). The reaction mixture was heated at 60 °C for 24 h and was diluted with ethyl acetate (25 mL), and washed with water (15 mL) and brine (15 mL). The organic layer was separated and dried over MgSO₄ and filtered. The solvent was removed using a rotary evaporator and the residue was subjected to column chromatography (silica gel, hexanes: ethyl acetate 60:40) to yield 2g as a yellow solid (0.14 g, 51%, m.p. 205.8-207.2 °C). ¹H-NMR (CDCl3, 300 MHz): δ 8.06–8.00 (m, 8H), 7.90 (s, 4H), 7.85 (d, 2H, J = 9.3 Hz), 7.77 (d, 2H, J = 7.8 Hz), 7.65 (s, 2H, triazole-H), 7.07 (s, 2H, Ar-OH), 6.90 (s, 4H, Ar-H), 6.65 (s, 4H, Ar-H), 6.13 (s, 4H, pyrene-CH2-triazole), 4.88 (s, 4H, -OCH2), 4.02 (d, 4H, Ar-CH2, J = 13.2 Hz, 3.07 (d, 4H, Ar-CH2, J = 13.2 Hz), 1.74-1.68 (m, 4H), 1.47 (s, 12H), 1.24 (s, 18H, 1.24)*t*-Bu), 1.02–0.95 (m, 6H), 0.94–0.89 (m, 4H), 0.86 (s, 18H, *t*-Bu). ¹³C-NMR (CDCl3, 75.4 MHz): δ 150.4, 149.5, 148.0, 147.0, 144.2, 141.4, 132.6, 131.6, 130.9, 130.3, 128.9, 128.7, 128.3, 127.6, 127.2, 126.9, 126.7, 125.5, 124.9, 124.8, 123.6, 123.5, 122.6, 121.8, 69.1, 52.1, 44.6, 38.2, 33.8, 33.7, 31.9, 31.7, 30.9, 29.5, 29.2, 28.1, 24.1. APCI(+) MS (m/z): 1420.9 $[M+1]^+$.



Figure S1. ¹H(300 MHz, CDCl₃, 293 K). and ¹³C –NMR (75 MHz, CDCl₃, 293 K) spectrums of 5.



Figure S2. ¹H(300 MHz, CDCl₃, 293 K). and ¹³C –NMR (75 MHz, CDCl₃, 293 K) spectrums of 6.



Selected Mass Spectrum Report



Figure S4. APCI(+) mass spectrum of 2g.



Figure S5. Geometry-optimized (ball-and-stick) structures of (a) host **2g**, (b) **2g** \supset **Fe**²⁺, (c) **2g** \supset **Zn**²⁺; (d) **2g** \supset **Hg**²⁺; (e) **2g** \supset **Cd**²⁺; (f) **2g** \supset **Pb**²⁺: *Left*: **5** and *Right*: **5** \supset **Fe**³⁺ complex. Colour code: Fe²⁺ = magenta; Zn²⁺ = light blue; Hg²⁺ = purple; Cd²⁺ = pink; Pb2+ = green triazole nitrogen = blue, hydrogen = white and oxygen = red.

Table S1. Selected parameters from the B3LYPD3/GenECP (gas phase) geometry optimized structures of 2, 3, and of the metal ion complexes of $2\mathbf{a}$ - \mathbf{g} as well as the experimentally-derived K_{asso} values with $2\mathbf{g}$.

		HOMO/		D(HOMO _{Host}	рца	Distances				
-	DE	LUMO gap	O Kassoc	- LUMO _{M2+})	DHA	O-M ²⁺ (Avg.)	N ₃ /N ₃ -M ²⁺ (Avg.)	N3-N3'	C1–C1'	C7- C7'
	kJ mol ⁻¹	eV	M ⁻¹ x10 ⁵	eV	0	(Å)	(Å)	(Å)	(Å)	(Å)
3	-	3.41	-		-77.6	-	-	6.14	4.16	3.77
2g	-	3.38	-		-61.0	-	-	6.00	4.31	5.98
2g:Fe ²⁺	-1647	1.29	0.377	-0.1260	-62.1	2.30	2.35	2.84	4.19	5.53
$2g:Zn^{2+}$	-1428	2.90	1.11	-0.1260	-68.2	2.32	2.35	3.08	4.80	6.33
2g:Pb ²⁺	-964.6	2.47	0.912	-0.1282	-91.0	2.72	2.73	3.83	6.31	6.92
$2g:Cd^{2+}$	-1225	2.89	1.48	-0.1258	-93.4	2.51	2.55	3.59	6.00	6.82
2g: Hg ²⁺	-1216	1.68	1.00	-0.1268	-94.6	2.59	2.62	3.73	6.24	6.88

Table S2. Selected parameters from the B3LYP/GenECP (gas phase) geometry optimized structures of 2a-g and 3.

Cmpd.	Opt energy	HOMO/LUMO	Distances				
	(kJ mole-1)	gap (eV)	DHA	N3-N3'(Å)	C1-C1'(Å)	C7-C7'(Å)	
2a	-1.091E+07	3.388	-92.3	5.708	3.811	3.128	
2b	-1.101E+07	3.448	-60.48	5.926	4.995	3.612	
2c	-1.111E+07	3.427	-66.79	5.979	4.721	4.422	
2d	-1.122E+07	3.335	-77.93	6.263	4.098	4.520	
2e	-1.132E+07	3.309	-79.72	6.002	4.284	5.511	
2f	-1.142E+07	3.370	-68.03	5.896	4.451	6.089	
2g	-1.153E+07	3.376	-61.05	5.998	4.313	5.983	
3	-1.019E+07	3.410	-77.61	6.144	4.156	3.773	



Figure S6. (a) Fluorescence titration spectra of **2g** $(2.02 \times 10^{-5} \text{ M})$ with additions of Zn(ClO₄)₂ (0-20.7 eqv.) in CH₃CN/ CHCl₃ (9:1,v/v). λ ex=330 nm; (b) 1:1 UV/Flu. Binding model for **2g** with Zn²⁺.



Figure S7. (a) Fluorescence titration spectra of **2g** $(2.02 \times 10^{-5} \text{ M})$ with additions of Cd(ClO₄)₂ (0-16.35 μ M) in CH₃CN/CHCl₃ (9:1,v/v). λ ex=330 nm; and (b) 1:1 UV/Flu. Binding model for **2g** with Cd²⁺.



Figure S8. (a) Fluorescence titration spectra of **2g** $(2.02 \times 10^{-5} \text{ M})$ with additions of Hg(ClO₄)₂ (0-13.92 μ M) in CH₃CN/CHCl₃ (9:1,v/v). λ ex=330 nm; and (b) 1:1 UV/Flu. Binding model for **2g** with Hg²⁺.



Figure S9. (a) Fluorescence titration spectra of **2g** $(2.02 \times 10^{-5} \text{ M})$ with additions of Pb(ClO₄)₂ (0-12.02 μ M) in CH₃CN/CHCl₃ (9:1,v/v). λ ex=330 nm; and (b) 1:1 UV/Flu. Binding model for **2g** with Pb²⁺.



Figure S10. (a) Fluorescence spectra of **2g** (2.02×10^{-5} M) upon addition of Fe(ClO₄)₂ (0-12.22 μ M) in CH₃CN/CHCl₃ (9:1,v/v). λ ex=330 nm; and (b) 1:1 UV/Flu. Binding model for **2g** with Fe²⁺.



Figure S11. (a) Fluorescence spectra of **2g** (2.02×10^{-5} M) upon addition of Ni(ClO₄)₂ (0-13.17 μ M) in CH₃CN/CHCl₃ (9:1,v/v). λ ex=330 nm; and (b) 1:1 UV/Flu. Binding model for **2g** with Ni²⁺.



Figure S12. (a) Fluorescence spectra of **2g** $(2.02 \times 10^{-5} \text{ M})$ upon addition of Mn(ClO₄)₂ $(0-22.22 \mu \text{M})$ in CH₃CN/CHCl₃ (9:1,v/v). $\lambda ex=330 \text{ nm}$; and (b) 1:1 UV/Flu. Binding model for **2g** with Mn²⁺.



Figure S13. (a) Fluorescence spectra of **2g** $(2.02 \times 10^{-5} \text{ M})$ upon addition of AgClO₄ (0-25.02 μ M) in CH₃CN/CHCl₃ (9:1,v/v). λ ex=330 nm; and (b) 1:1 UV/Flu. Binding model for **2g** with Ag⁺.



Figure S14. Geometry-optimized structures of **2a-f**. The atom labels that are used for the distances (Å) referred to in Tables 1 (main Text) and S2 are also shown in Figure 1 (main Text). The magenta-highlighted atoms are the pyrenes bridging carbon atoms.

References

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