

Thiacalixarenes with sulfur functionalities at lower rim: heavy metal ion binding in solution and 2D-confined space

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Electronic Supplementary Information

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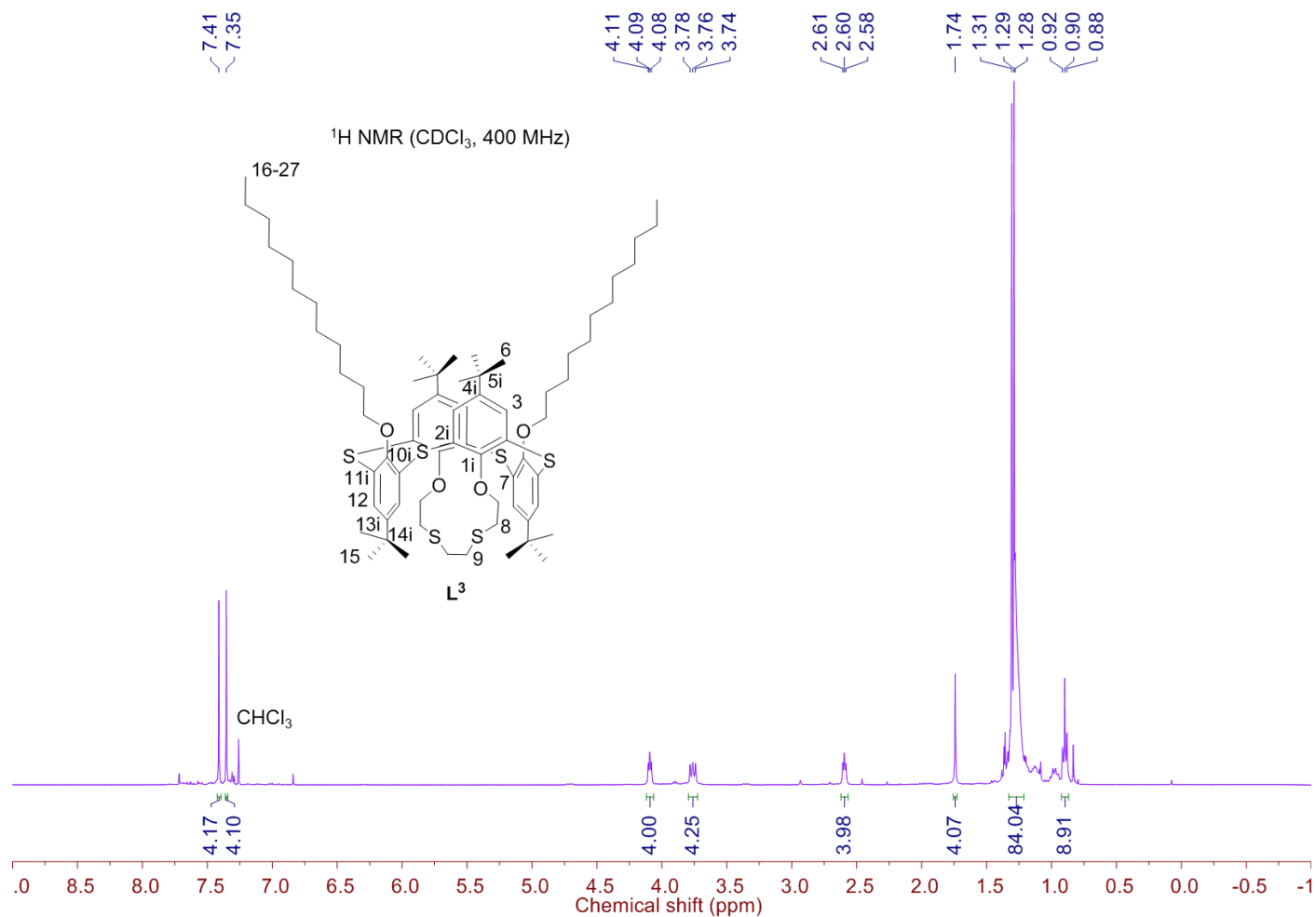


Figure S1. ¹H NMR spectrum of compound **L³** (CDCl₃, 400 MHz, 303 K).

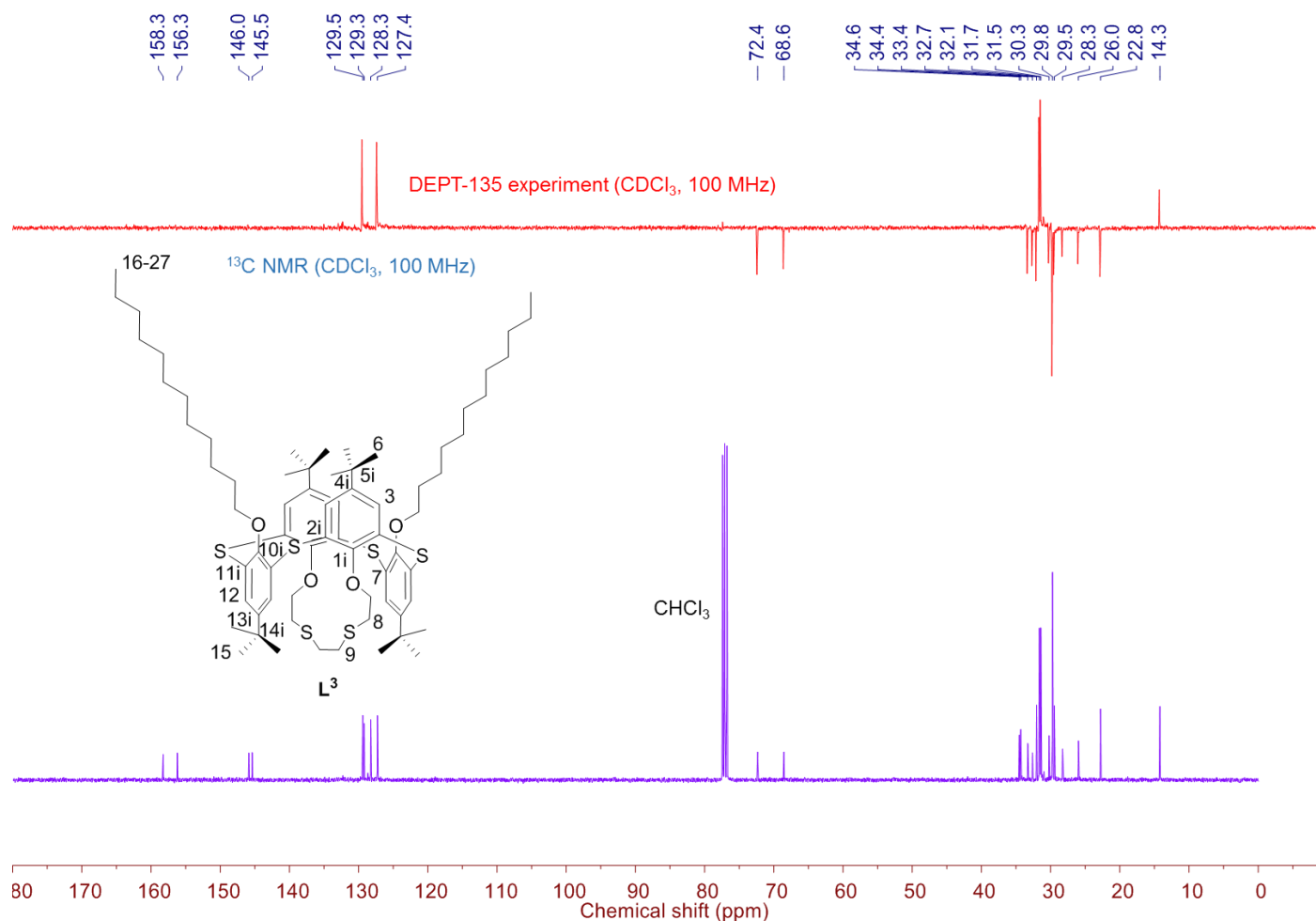


Figure S2. ¹³C NMR spectrum and DEPT-135 experiment of compound **L³** (CDCl₃, 100 MHz, 303 K).

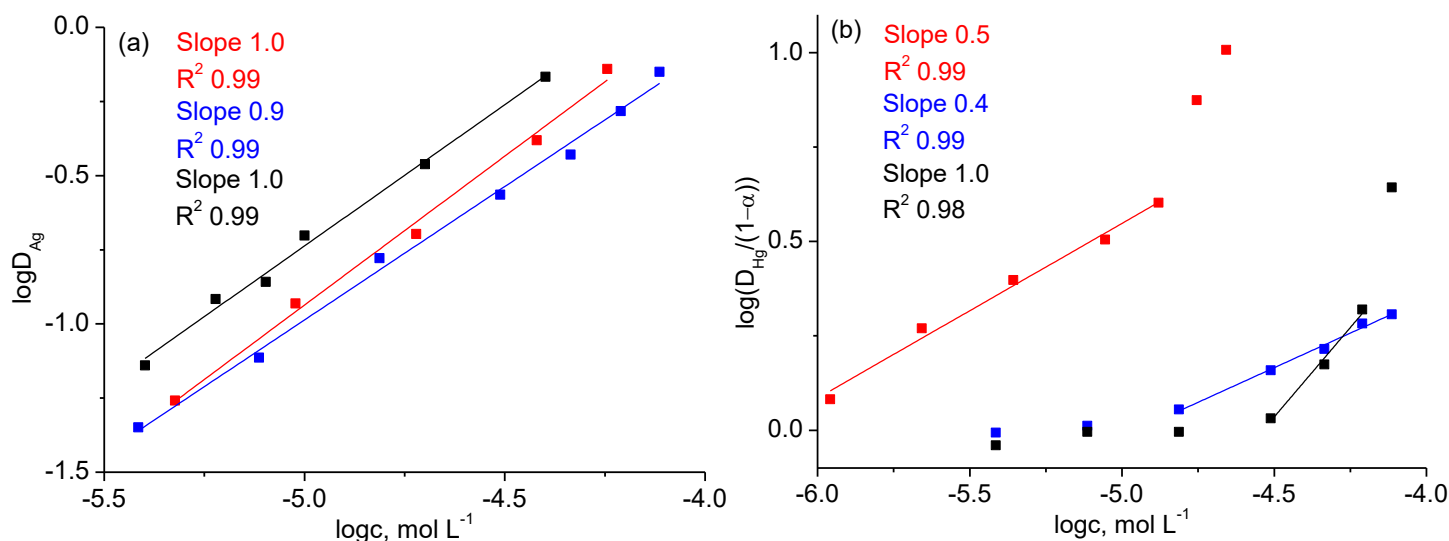


Figure S3. Plots of (a) $\log D_{\text{Ag}}$ and (b) $\log(D_{\text{Hg}}/(1-\alpha))$ against $\log c$ for thioethers L^2 (red line), L^3 (blue line), and L^4 (black line) in the DCM–H₂O system ($c(\text{AgPic}) = 1 \times 10^{-4} \text{ M}$ and $c(\text{HgPic}_2) = 1 \times 10^{-4} \text{ M}$ (ligand L^2) or $5 \times 10^{-5} \text{ M}$ (ligands L^3 and L^4).

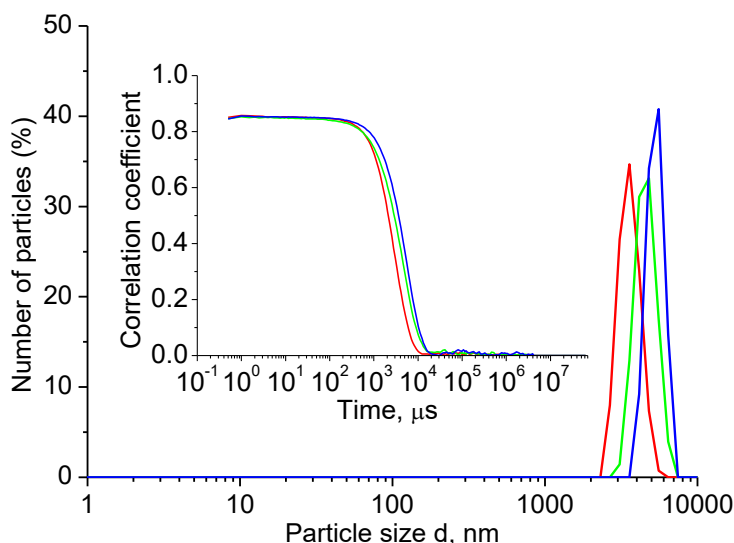


Figure S4. Number-averaged particle size distribution and corresponding correlograms of CH₂Cl₂ phase after mixing with aqueous phase containing Hg(NO₃)₂ dissolved in tris·HCl buffer in picric acid (blue curves) and CH₂Cl₂ phase with dissolved compound L^2 after mixing with aqueous phase containing picric acid and tris·HCl buffer (red curve) and aqueous phase containing Hg(NO₃)₂ (green curve).

Table S1. Crystallographic parameters of the metal complexes

Formula	$[\text{Ag}_2\text{L}^2](\text{ClO}_4)_2$, $\text{C}_{92}\text{H}_{120}\text{Ag}_2\text{O}_8\text{S}_{12}$, 2(ClO_4)	$[\text{Ag}_2\text{L}^2(\text{ClO}_4)_2]_n$, $\text{C}_{46}\text{H}_{60}\text{Ag}_2\text{Cl}_2\text{O}_{12}\text{S}_6$, 2(CHCl_3)	$[\text{Hg}_2\text{L}^4\text{Cl}_4]$, $\text{C}_{92}\text{H}_{116}\text{Cl}_4\text{Hg}_2\text{O}_8\text{S}_{12}$
Molecular weight	2153.23	1522.67	2277.54
Crystal system	triclinic	orthorhombic	triclinic
Space group	<i>P</i> -1	<i>Pbca</i>	<i>P</i> -1
<i>a</i> (Å)	12.200(2)	18.075(4)	10.115(2)
<i>b</i> (Å)	15.200(3)	19.726(4)	15.338(3)
<i>c</i> (Å)	16.680(3)	35.121(7)	19.017(4)
α (deg)	76.01(3)	90	96.48(3)
β (deg)	77.06(3)	90	101.05(3)
γ (deg)	75.59(3)	90	99.55(3)
<i>V</i> (Å ³)	2862.5(12)	12522(4)	2823.4(11)
<i>Z</i>	1	8	1
Colour	Colourless	Colourless	Colourless
Crystal dim (mm ³)	0.03 x 0.02 x 0.02	0.03 x 0.02 x 0.02	0.03 x 0.02 x 0.02
<i>D</i> _{calc} (gcm ⁻³)	1.249	1.615	1.339
<i>F</i> (000)	1120	6176	7180
μ (mm ⁻¹)	0.740	1.333	0.632
Wavelength (Å)	0.7450	0.7450	0.80246
Number of data measurements	48689	129153	44088

Number of data with $I > 2\sigma(I)$	15666 [R(int) = 0.0420]	17272 [R(int) = 0.0410]	12340 [R(int) = 0.1087]
R (%)	5.43	3.08	8.01
R_w (%)	15.84	8.41	22.27
GOF	1.042	1.078	1.036
Largest diff. peak and hole ($e\text{\AA}^{-3}$)	1.380 and -1.683	1.700 and -1.382	2.424 and -2.555

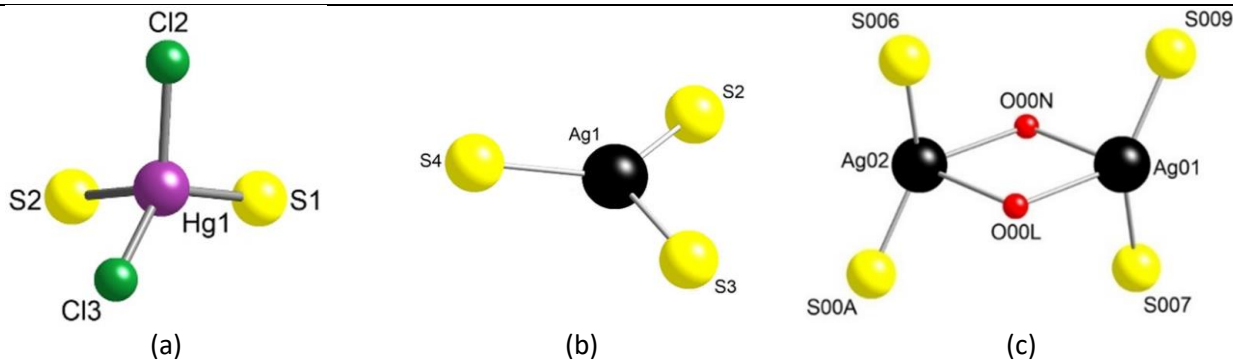


Figure S5. Coordination environment of metal ions in (a) $[\text{Hg}_2\text{L}^4\text{Cl}_4]$, (b) $[\text{Ag}_2\text{L}^2_2](\text{ClO}_4)_2$, and (c) $[\text{Ag}_2\text{L}^2(\text{ClO}_4)_2]_n$.

Table S2. Bond distances and angles for metal coordination environment in $[\text{Hg}_2\text{L}^4\text{Cl}_4]$, $[\text{Ag}_2\text{L}^2_2](\text{ClO}_4)_2$, and $[\text{Ag}_2\text{L}^2(\text{ClO}_4)_2]_n$

$[\text{Hg}_2\text{L}^4\text{Cl}_4]$	$[\text{Ag}_2\text{L}^2_2](\text{ClO}_4)_2$	$[\text{Ag}_2\text{L}^2(\text{ClO}_4)_2]_n$	
$d(\text{Hg1-S1}) = 2.579(8) \text{ \AA}$	$d(\text{Ag1-S2}) = 2.520(6) \text{ \AA}$	$d(\text{Ag01-S007}) = 2.586(7) \text{ \AA}$	$\angle \text{S007Ag01S009} = 135.38(6)^\circ$
$d(\text{Hg1-S2}) = 2.789(5) \text{ \AA}$	$d(\text{Ag1-S3}) = 2.553(1) \text{ \AA}$	$d(\text{Ag01-S009}) = 2.472(1) \text{ \AA}$	$\angle \text{S007Ag01O00N} = 91.32(0)^\circ$
$d(\text{Hg1-Cl2}) = 2.397(8) \text{ \AA}$	$d(\text{Ag1-S4}) = 2.570(2) \text{ \AA}$	$d(\text{Ag01-O00L}) = 2.492(2) \text{ \AA}$	$\angle \text{S009Ag01O00L} = 131.23(4)^\circ$
$d(\text{Hg1-Cl3}) = 2.340(0) \text{ \AA}$	$\angle \text{S4Ag1S2} = 132.59(7)^\circ$	$d(\text{Ag01-O00N}) = 2.681(8) \text{ \AA}$	$\angle \text{S006Ag02O00N} = 90.72(4)^\circ$
$\angle \text{Cl2Hg1S1} = 98.26(3)^\circ$	$\angle \text{S2Ag1S3} = 115.00(0)^\circ$	$d(\text{Ag02-S00A}) = 2.480(2) \text{ \AA}$	$\angle \text{S006Ag02O00L} = 88.10(6)^\circ$
$\angle \text{S1Hg1Cl3} = 127.51(2)^\circ$	$\angle \text{S3Ag1S4} = 112.03(7)^\circ$	$d(\text{Ag02-S006}) = 2.585(6) \text{ \AA}$	$\angle \text{O00NAg02O00L} = 70.26(0)^\circ$
$\angle \text{Cl3Hg1S2} = 101.22(6)^\circ$		$d(\text{Ag02-O00L}) = 2.739(3) \text{ \AA}$	$\angle \text{O00LAg02S00A} = 91.84(4)^\circ$
$\angle \text{S2Hg1Cl2} = 102.03(8)^\circ$		$d(\text{Ag02-O00N}) = 2.514(2) \text{ \AA}$	$\angle \text{S00AAg02S006} = 135.73(0)^\circ$
$\angle \text{Cl2Hg1Cl3} = 130.54(5)^\circ$		$\angle \text{S009Ag01O00N} = 91.02(2)^\circ$	$\angle \text{S00AAg02O00N} = 130.58(7)^\circ$
$\angle \text{S1Hg1S2} = 83.00(4)^\circ$		$\angle \text{O00NAg01O00L} = 71.55(0)^\circ$	$\angle \text{Ag01O00NAg02} = 109.67(2)^\circ$
		$\angle \text{O00LAg01S007} = 91.37(0)^\circ$	$\angle \text{Ag01O00LAg02} = 108.51(9)^\circ$

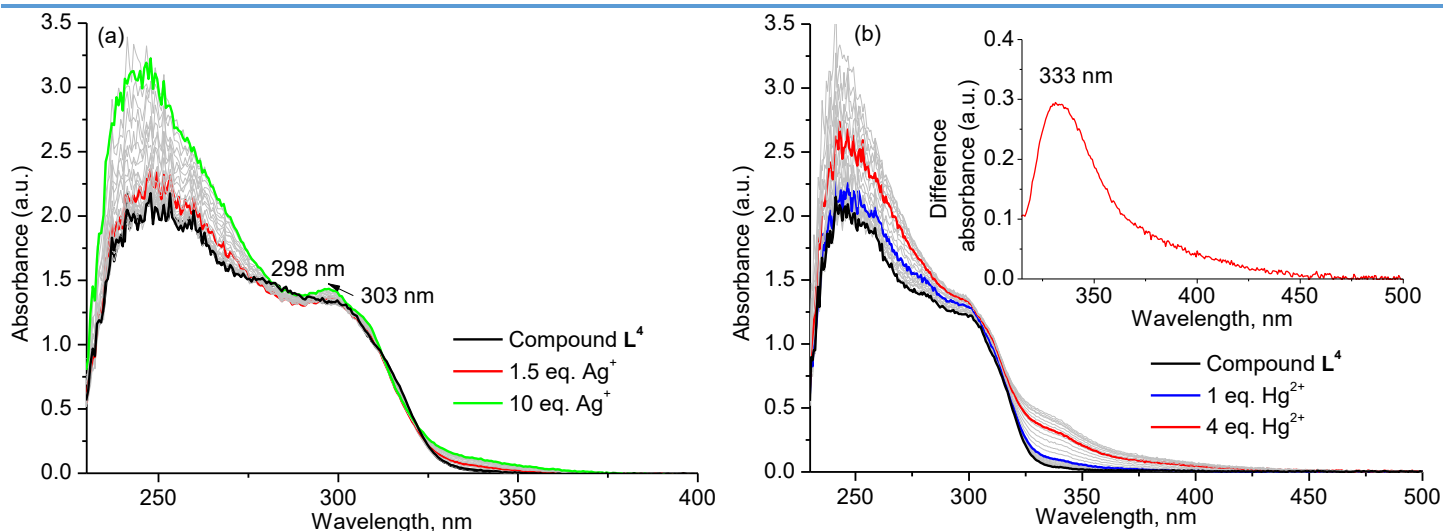


Figure S6. Evolution of UV/Vis absorption spectra of compound L^4 ($c = 1 \times 10^{-5} \text{ M}$ in 10:1 CH_2Cl_2 -MeOH) on addition of (a) Ag^+ and (b) Hg^{2+} as perchlorates. Inset shows difference spectrum of ligand L^4 and its Hg complex.

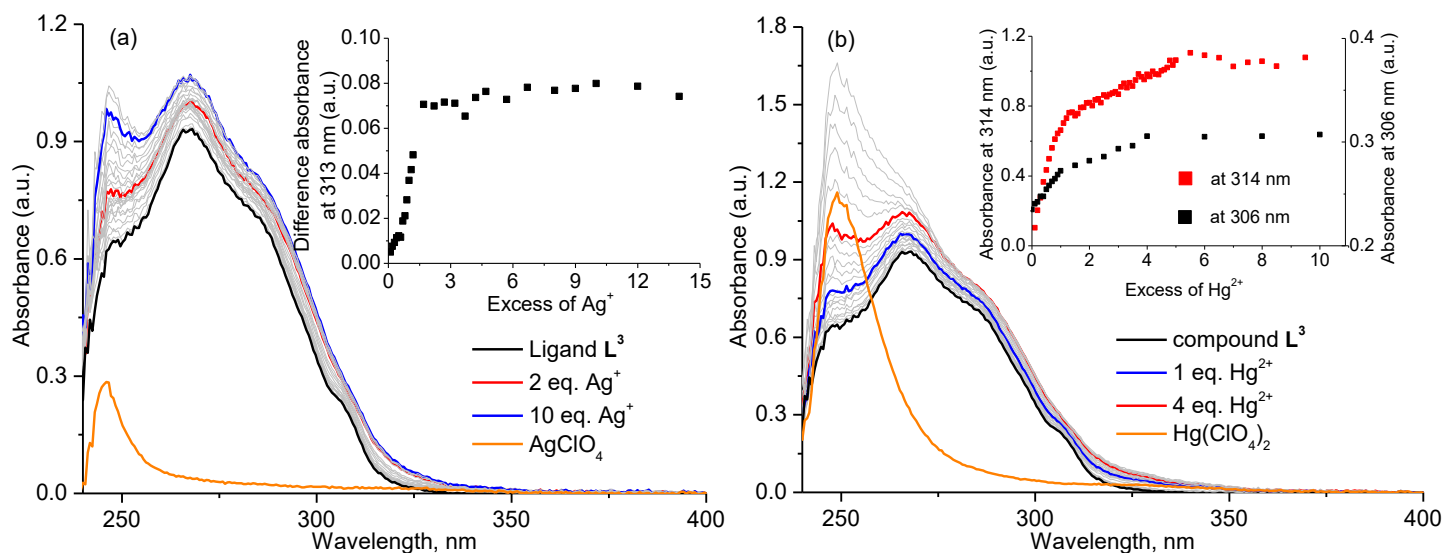


Figure S7. Evolution of UV/Vis absorption spectra of compound L^3 ($c = 1 \times 10^{-5} M$ in 10:1 CH_2Cl_2 -MeOH) on addition of Ag^+ and Hg^{2+} as perchlorates. Insets show scatter plots of titration.

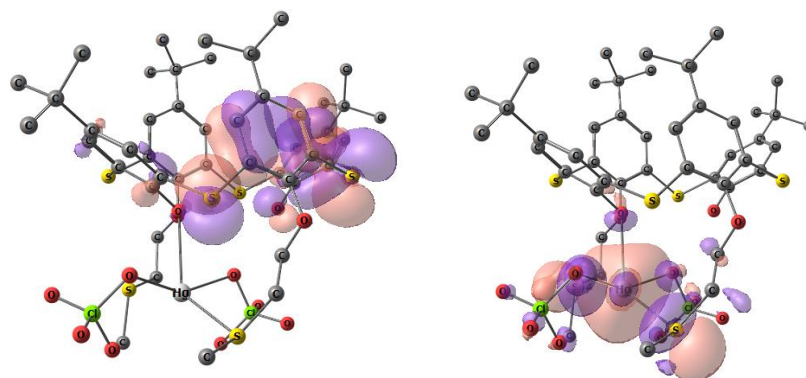


Figure S8. Frontier molecular orbitals contributing to low-energy absorption bands of L^2 -Hg-a complex: HOMO (left) and LUMO (right).

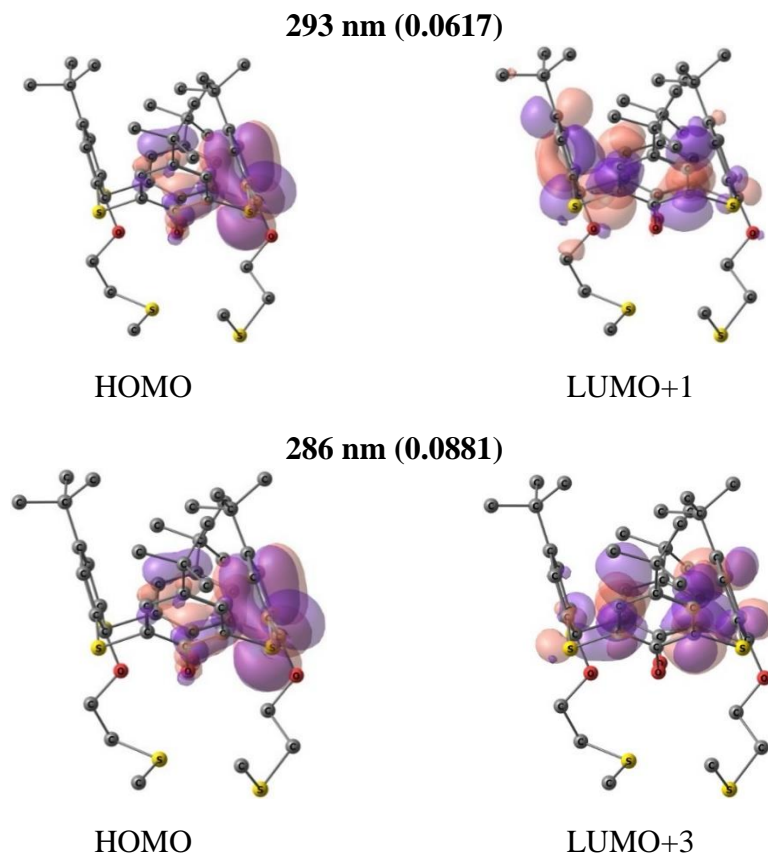


Figure S9. Frontier molecular orbitals contributing to low-energy absorption bands of ligand L^2 .

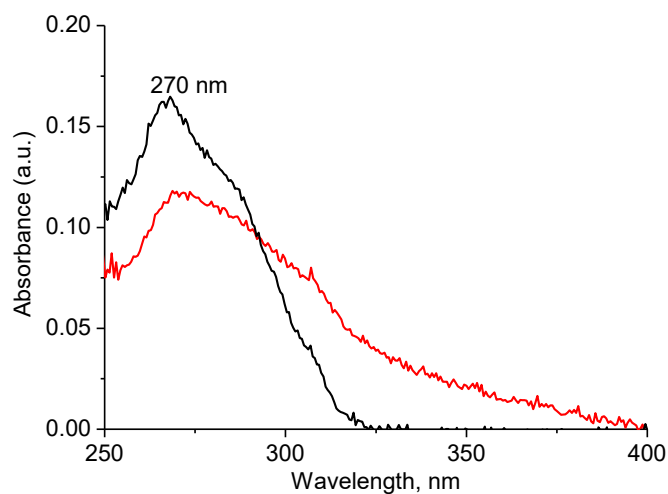
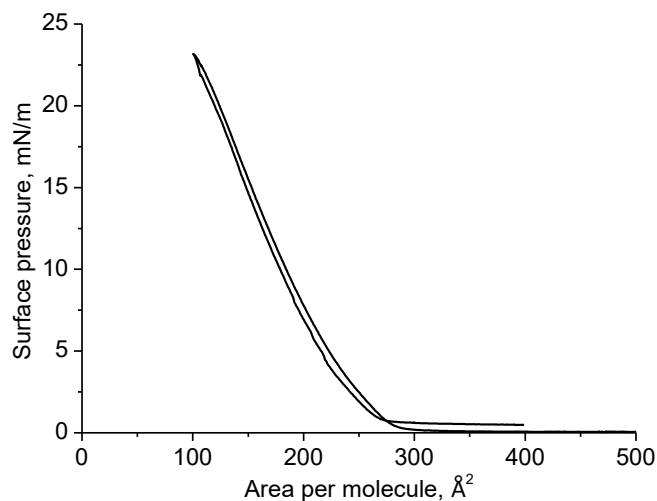


Figure S10. Monolayer compression–expansion cycle of compound L^4 at the air–water interface ($c = 5 \times 10^{-5} M$ in $CHCl_3$).

Figure S11. UV/Vis spectra of compound L^3 in $CHCl_3$ ($c = 2 \times 10^{-6} M$) (black curve) and at air–water interface ($\pi = 17$ mN/m) (red curve).

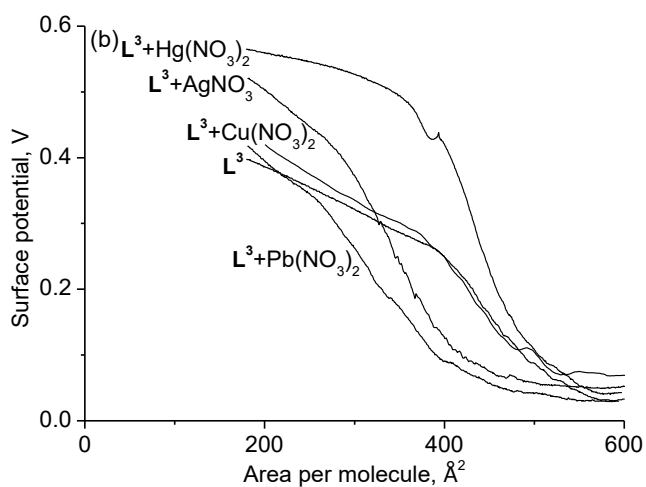
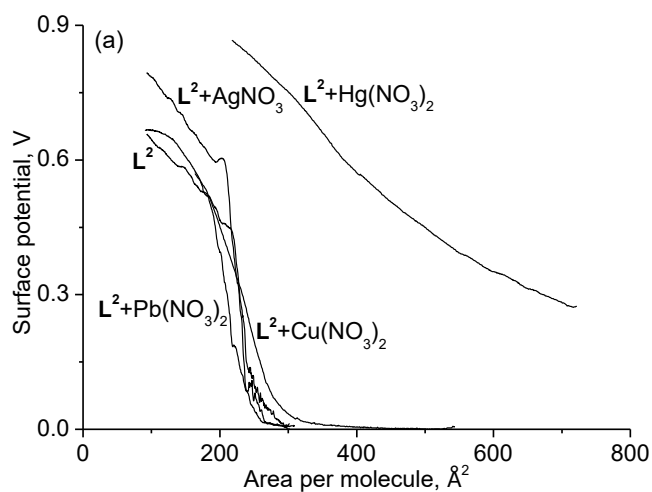


Figure S12. SPOT–A isotherms of ligands (a) L^2 and (b) L^3 ($c = 5 \times 10^{-5} M$ in $CHCl_3$) over deionized water or salt solution.

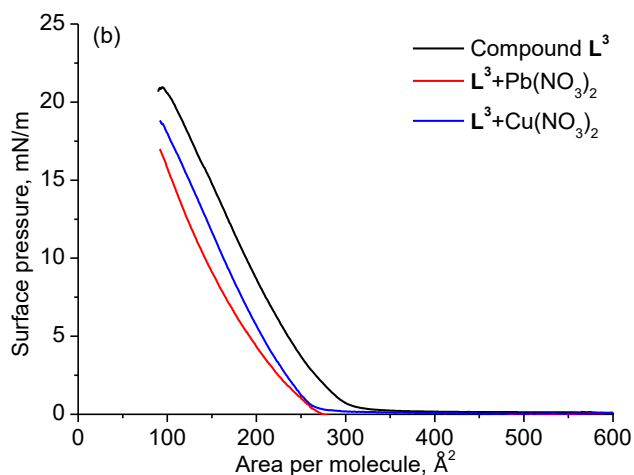
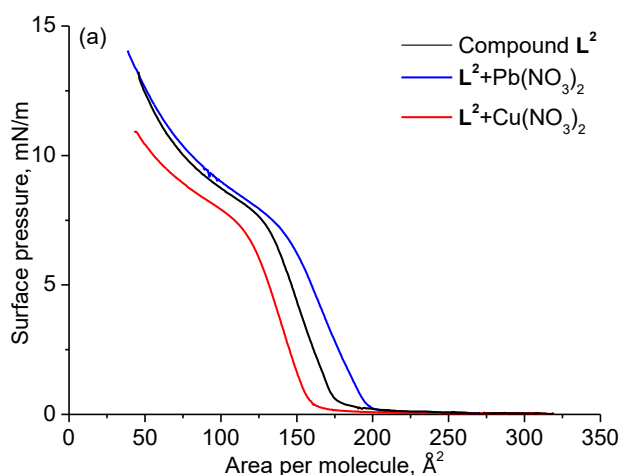


Figure S13. π –A isotherms of ligands L^2 and L^3 over deionized or salt water subphase ($c = 5 \times 10^{-5} M$ in $CHCl_3$).

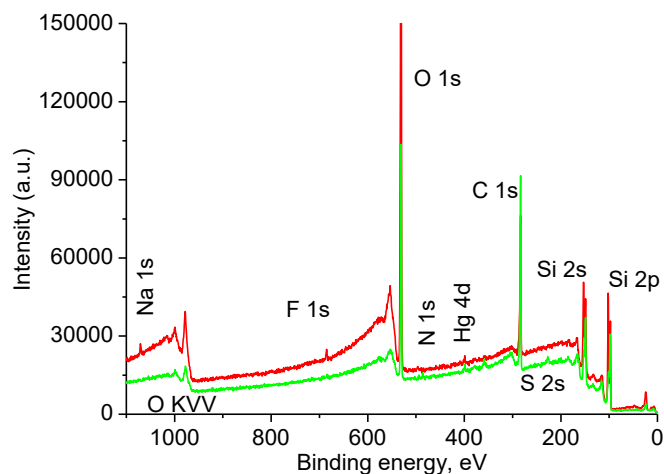


Table S3. Main characteristics of the components of XPS spectrum of Langmuir–Blodgett film-coated quartz

Name, state	Position, eV	Intensity, a.u.	FWHM, eV
Si2p _{3/2} , Si ⁰	99.34	8410	0.60
Si2p _{1/2} , Si ⁰	99.95	4205	0.50
Si ⁺	100.30	1657	0.84
Hg4f _{7/2}	101.16	2910	1.18
Si ²⁺	101.86	940	0.97
Si ⁴⁺	103.20	8173	1.52
Hg4f _{5/2}	105.42	2216	1.19

Figure S14. XPS spectra of bare quartz (red curve) and LB film on quartz formed by monolayer of compound **L**³ over 10^{−4} M Hg(ClO₄)₂ solution (green curve).

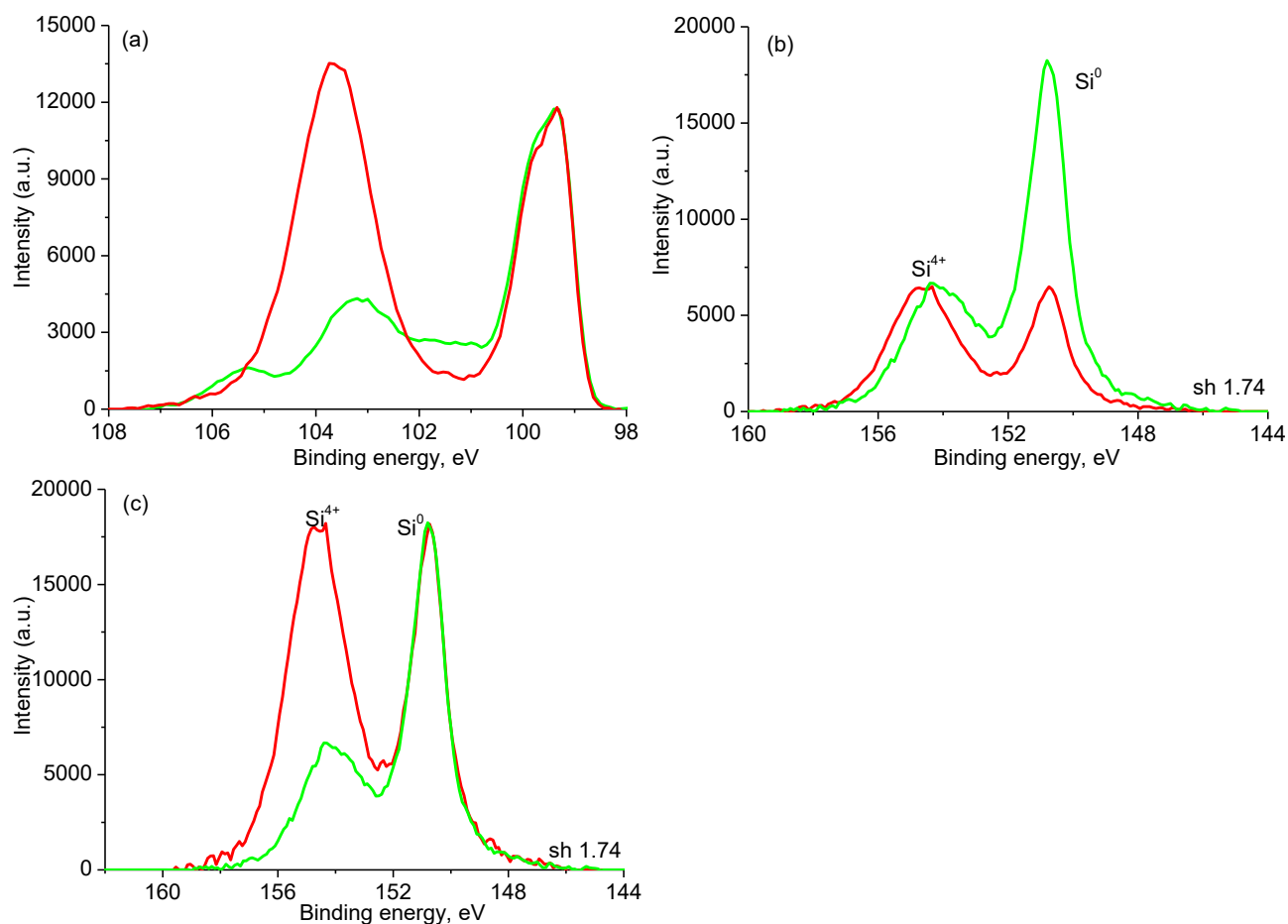


Figure S15. Partial XPS spectra of (a) Si2p and (b,c) Si2s regions of bare quartz (red curve) and LB film of compound **L**³ with Hg(ClO₄)₂ (green curve) normalized by the intensity of (a,c) low- and (b) high-energy peaks.