Supplementary Information

Single and double crown macrocyclic derivatives of cyclotriphosphazene as receptors of silver (I) ions

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Table S1. Crystallographic data for compound **L2**.

	compound **L2**
Empirical formula	$C_{26}H_{52}N_5O_{10}P_3$
Molecular weight	687.63
Size (mm)	0.08 × 0.11 × 0.12
Crystal system	orthorhombic
Space group	P21212
a[Å]	12.4915(2)
b[Å]	13.3518(2)
c[Å]	9.9705(1)
V[Å^3]	1662.92(4)
Z/ d_x[g cm^{-3}]	2/1.373
μ[cm^{-1}]	0.239
λ[Å]	0.71073
max θ[°]	25.425
No. of measured reflections	27358
No. of unique reflections	8948
$R_{(int)}$	0.0234
No. of observed reflns (I>2 σ(I))	8348
Data/restraints/parameters	8948/0/200
R_1(obsd data)	0.0273
R_1(all data)	0.0317
Goodness-of-fit on F^2	1.11
largest difference peak and hole [e/Å^3]	0.485/-0.434

Table S2. The values of stepwise stability constants taken from the previous paper[19].

	Tetrapyrrolidinyl-PNP-lariat ether		Tetramorpholinyl-PNP-lariat ether	
Complex form	log β in methanol	log β in acetonitrile	log β in methanol	log β in acetonitrile
$Ag^+ + L \rightarrow AgL^+$	4.38 ± 0.01	2.73 ± 0.01	3.20 ± 0.02	1.88 ± 0.01
$AgL^+ + L \rightarrow AgL_2^+$	3.14 ± 0.03	3.62 ± 0.01	3.38 ± 0.04	2.90 ± 0.01
$AgL^+ + Ag^+ \rightarrow Ag_2L^{2+}$	2.71 ± 0.02	2.07 ± 0.02	-	-

Table S3. ^{1}H NMR and ^{13}C NMR data in CD_3OD and CD_3CN for uncomplexed ligand **L1** – and after adding silver ion with the Ag:L molar ratio 0.5:1, 1:1 and 2:1

	Methanol		**Acetonitrile**	
	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR
L1	4.01 (2H, CH_2OP, m)	65.3	3.90 (2H, CH_2OP, m)	64.7
	3.94(2H, CH_2OP, m)	65.3	3.81(2H, CH_2OP, m)	64.7
	3.71 (2H, CH_2C, m)	71.2	3.62 (2H, CH_2C, m)	70.9
	3.65 (6H, CH_2C, m)	71.8	3.58 (6H, CH_2C, m)	71.4
	3.60 (4H, CH_2C, m)	71.7	3.55 (4H, CH_2C, m)	71.3
	3.07 (16H, CH_2N, m)	46.6	2.98 (16H, CH_2N, m)	46.1
	1.57 (8H, CH_2C, m)	25.9	1.53 (8H, CH_2C, m)	25.8
	1.53 (16H, CH_2C, m)	27.3	1.47 (16H, CH_2C, m)	27.2
L1 + 0.5 Ag	4.08 (2H, CH_2OP, m)	66.1	3.97 (2H, CH_2OP, m)	65.5
	3.99 (2H, CH_2OP, m)	66.1	3.90(2H, CH_2OP, m)	65.5
	3.76 (2H, CH_2C, m)	71.3	3.66 (2H, CH_2C, m)	70.8
	3.67 (6H, CH_2C, m)	71.4	3.58 (6H, CH_2C, m)	71.3
	3.63 (4H, CH_2C, m)	71.4	3.55 (4H, CH_2C, m)	71.2
	3.11 (16H, CH_2N, m)	46.7	3.04 (16H, CH_2N, m)	46.3
	1.60 (8H, CH_2C, m)	25.9	1.55 (8H, CH_2C, m)	25.6
	1.56 (16H, CH_2C, m)	27.3	1.50 (16H, CH_2C, m)	27.1
L1 + 1 Ag	4.15 (2H, CH_2OP, m)	66.6	4.00 (2H, CH_2OP, m)	65.8
	4.00(2H, CH_2OP, m)	66.6	3.93(2H, CH_2OP, m)	65.8
	3.81 (2H, CH_2C, m)	71.0	3.68 (2H, CH_2C, m)	70.7
	3.71 (6H, CH_2C, m)	70.5	3.58 (6H, CH_2C, m)	71.2
	3.67 (4H, CH_2C, m)	70.2	3.55 (4H, CH_2C, m)	70.9
	3.14 (8H, CH_2N, m)	46.8	3.05 (16H, CH_2N, m)	46.3
	3.09 (8H, CH_2N, m)	46.6		25.5
	1.61 (8H, CH_2C, m)	25.8	1.56 (8H, CH_2C, m)	27.0
	1.56 (16H, CH_2C, m)	27.3	1.51 (16H, CH_2C, m)	
L1 + 2 Ag	4.22 (2H, CH_2OP, m)	67.0	4.02 (2H, CH_2OP, m)	65.9
	4.06(2H, CH_2OP, m)	67.0	3.93(2H, CH_2OP, m)	65.9
	3.85 (2H, CH_2C, m)	70.8	3.69 (2H, CH_2C, m)	70.6
	3.75 (6H, CH_2C, m)	69.4	3.59 (6H, CH_2C, m)	71.1
	3.69 (4H, CH_2C, m)	69.9	3.57 (4H, CH_2C, m)	71.1
	3.18 (8H, CH_2N, m)	47.6	3.06 (16H, CH_2N, m)	46.3
	3.11 (8H, CH_2N, m)	46.7	1.56 (8H, CH_2C, m)	25.5
	1.61 (8H, CH_2C, m)	25.6	1.51 (16H, CH_2C, m)	26.9
	1.57 (16H, CH_2C, m)	27.2		

Table S4. ^{1}H NMR and ^{13}C NMR data in CD_3OD and CD_3CN for uncomplexed ligand **L2** – and after adding silver ion with the Ag:L molar ratio 0.5:1, 1:1, 2:1, 3:1 and 4:1

	Methanol		**Acetonitrile**	
	^{1}H NMR	^{13}C NMR	^{1}H NMR	^{13}C NMR
L2	4.37 (2H, $P(CH_2O)_2$, m)	66.7	4.34 (2H, $P(CH_2O)_2$, m)	66.1
	4.04 (2H, $P(CH_2O)_2$, m)	66.7	3.93 (2H, $P(CH_2O)_2$, m)	66.1
	4.33 (2H, CH_2OP, m)	64.4	4.26 (2H, CH_2OP, m)	64.2
	3.68 (2H, CH_2OP, m)	64.4	3.62 (2H, CH_2OP, m)	64.2
	3.74 (22H, CH_2C, m)	71.8,71.7,71.5, 71.3,71.1	3.68 (22H, CH_2C, m)	71.4,71.2,71.1, 70.9,70.5
	3.51 (2H, CH_2C, m)	70.1	3.45 (2H, CH_2C, m)	69.7
	3.14 (8H, CH_2N, m)	46.6	3.10 (8H, CH_2N, m)	46.2
	1.57 (4H, CH_2C, m)	25.9	1.54 (4H, CH_2C, m)	25.6
	1.53 (8H, CH_2C, m)	27.2	1.47 (8H, CH_2C, m)	27.0
L2 + 0.5 Ag	4.37 (2H, $P(CH_2O)_2$, m)	66.9	4.34 (2H, $P(CH_2O)_2$, m)	66.9
	4.07 (2H, $P(CH_2O)_2$, m)	66.9	4.06 (2H, $P(CH_2O)_2$, m)	66.9
	4.33 (2H, CH_2OP, m)	64.6	4.22 (2H, CH_2OP, m)	64.9
	3.75 (2H, CH_2OP, m)	64.6	3.69 (2H, CH_2OP, m)	64.9
	3.77 (22H, CH_2C, m)	71.8,71.6,71.4,71.1	3.70 (22H, CH_2C, m)	71.3,71.2,71.1,70.4
	3.52 (2H, CH_2C, m)	70.2	3.49 (2H, CH_2C, m)	70.1
	3.15 (8H, CH_2N, m)	46.6	3.11 (8H, CH_2N, m)	46.2
	1.58 (4H, CH_2C, m)	25.9	1.55 (4H, CH_2C, m)	25.5
	1.54 (8H, CH_2C, m)	27.2	1.49 (8H, CH_2C, m)	26.9
L2 + 1 Ag	4.38 (2H, $P(CH_2O)_2$, m)	67.1	4.35 (2H, $P(CH_2O)_2$, m)	67.7
	4.10 (2H, $P(CH_2O)_2$, m)	67.1	4.17 (2H, $P(CH_2O)_2$, m)	67.7
	4.32 (2H, CH_2OP, m)	64.8	4.19 (2H, CH_2OP, m)	65.6
	3.82 (2H, CH_2OP, m)	64.8	3.82 (2H, CH_2OP, m)	65.6
	3.78 (22H, CH_2C, m)	71.8,71.6,71.4,70.9	3.72 (22H, CH_2C, m)	71.6,71.3,71.2,70.6
	3.57 (2H, CH_2C, m)	70.2	3.54 (2H, CH_2C, m)	70.3
	3.16 (8H, CH_2N, m)	46.6	3.11 (8H, CH_2N, m)	46.3
	1.59 (4H, CH_2C, m)	25.8	1.56 (4H, CH_2C, m)	25.4
	1.55 (8H, CH_2C, m)	27.2	1.50 (8H, CH_2C, m)	26.9
L2 + 2 Ag	4.41 (2H, $P(CH_2O)_2$, m)	68.6	4.35 (2H, $P(CH_2O)_2$, m)	68.2
	4.29 (2H, $P(CH_2O)_2$, m)	68.6	4.22 (2H, $P(CH_2O)_2$, m)	68.2
	4.30 (2H, CH_2OP, m)	66.4	4.19 (2H, CH_2OP, m)	66.2
	3.94 (2H, CH_2OP, m)	66.4	3.90 (2H, CH_2OP, m)	66.2
	3.79 (22H, CH_2C, m)	72.1,71.8,71.7,71.0	3.71 (22H, CH_2C, m)	71.6,71.4,71.2,70.7
	3.65 (2H, CH_2C, m)	70.8	3.58 (2H, CH_2C, m)	70.4
	3.18 (8H, CH_2N, m)	46.8	3.12 (8H, CH_2N, m)	46.4
	1.60 (4H, CH_2C, m)	25.6	1.57 (4H, CH_2C, m)	25.3
	1.56 (8H, CH_2C, m)	27.2	1.51 (8H, CH_2C, m)	26.9
L2 + 3 Ag	4.47 (2H, $P(CH_2O)_2$, m)	69.5	4.36 (2H, $P(CH_2O)_2$, m)	68.6
	4.40 (2H, $P(CH_2O)_2$, m)	69.5	4.28 (2H, $P(CH_2O)_2$, m)	68.6
	4.34 (2H, CH_2OP, m)	67.4	4.21 (2H, CH_2OP, m)	66.6
	4.06 (2H, CH_2OP, m)	67.4	3.95 (2H, CH_2OP, m)	66.6
	3.80 (22H, CH_2C, m)	72.3,71.9,71.8,71.3	3.72 (22H, CH_2C, m)	71.6,71.4,71.2,70.9
	3.70 (2H, CH_2C, m)	70.9	3.61 (2H, CH_2C, m)	70.5
	3.20 (8H, CH_2N, m)	47.0	3.14 (8H, CH_2N, m)	46.5
	1.62 (4H, CH_2C, m)	25.5	1.58 (4H, CH_2C, m)	25.2
	1.57 (8H, CH_2C, m)	27.1	1.52 (8H, CH_2C, m)	26.8
L2 + 4 Ag	4.47 (2H, $P(CH_2O)_2$, m)	69.7	4.36 (2H, $P(CH_2O)_2$, m)	68.7
	4.43 (2H, $P(CH_2O)_2$, m)	69.7	4.30 (2H, $P(CH_2O)_2$, m)	68.7
	4.35 (2H, CH_2OP, m)	67.7	4.21 (2H, CH_2OP, m)	66.7
	4.10 (2H, CH_2OP, m)	67.7	3.96 (2H, CH_2OP, m)	66.7
	3.81 (22H, CH_2C, m)	72.2,71.9,71.8,71.3	3.72 (22H, CH_2C, m)	71.6,71.4,71.2,70.9
	3.71 (2H, CH_2C, m)	70.9	3.62 (2H, CH_2C, m)	70.5
	3.21 (8H, CH_2N, m)	47.0	3.14 (8H, CH_2N, m)	46.5
	1.63 (4H, CH_2C, m)	25.4	1.58 (4H, CH_2C, m)	25.2
	1.59 (8H, CH_2C, m)	27.1	1.52 (8H, CH_2C, m)	26.8

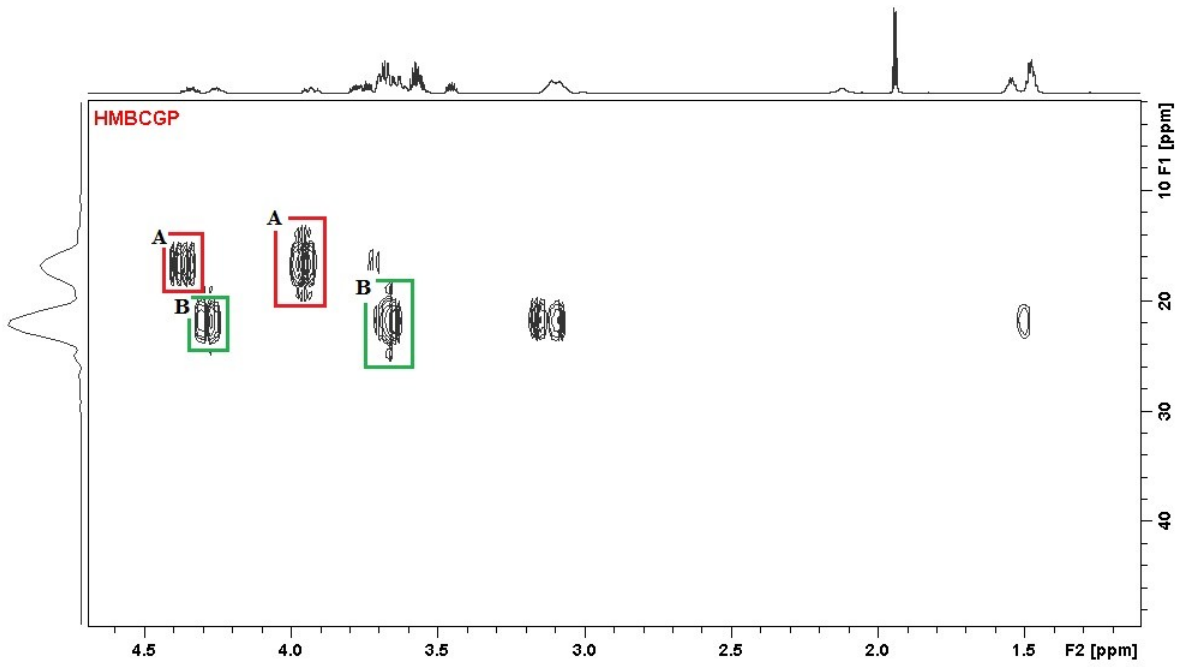
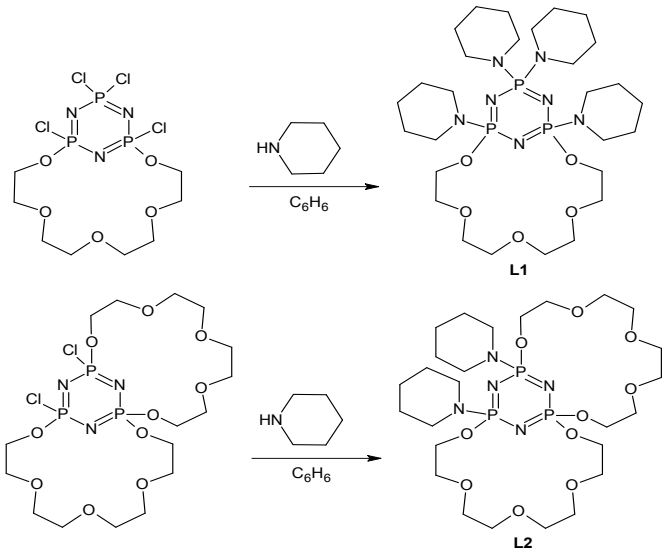


Fig.S1 $^{1}H - ^{31}P$ HMBC spectrum in CD_3CN for L2



Scheme S1 Syntheses of **L1** and **L2** ligands