Supplementary Information

Structure-Alkali Metal Cation Complexation Relationships for Macrocyclic PNP-Lariat Ether Ligands

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Table S2 Combustion analysis and ^{1}H NMR spectral data for monoaryloxy-subsititued PNP-lariat Ethers **3c-f**.

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Table S4 Combustion analysis and ^{1}H NMR spectral data for tetraaryloxy-substituted PNP-lariat ethers **4c-f**.

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Table S1 ^{31}P NMR spectral data for monoaryloxy-substituted PNP-lariat ethers **3c-f**.

	$^{31}P\{-^{1}H\}$ NMR, AMX spin system						$^{31}P\{=^{1}H\}$ NMR		
	δ_P, ppm[a]			J_{P-P}, Hz[b]			J_{P-H}, Hz		
Compound	P_A	P_M	P_X	A-M	A-X	M-X	P_AH	P_MH	P_XH
3c	5.90	27.60	21.10	75.0	70.4	77.3	12.3[c]	[d]	25.8[e]
3d	6.40	27.30	21.30	73.5	68.6	80.8	12.4[c]	[d]	23.5[e]
3e	6.46	27.48	20.64	75.8	70.7	80.6	12.5		23.6[e]
3f	5.65	27.32	20.86	77.7	70.4	79.8	12.6[e]		24.5[e]

[a]AMX spin system: P_a = P(OCH$_2$~)[OAr(z)]; P_M = PCl_2; P_X = P(OCH$_2$~)Cl. [b]J_{P-P} values calculated according to ref. 27. [c]For each peak of the double doublet split into triplets. [d]No proton coupling was evident. [e]For each peak of the double doublet split into quintets.

Table S2 Combustion analysis and ^{1}H NMR spectral data for monoaryloxy-substituted PNP-lariat ethers **3c-f**.

Formula	Elemental analysis, %[a] C	H	N	^{1}H NMR δ_H, ppm[b] (CH_2) OP	(CH_2) OC	$(CH)_{Ar}$	CHO	CH_3	(CH_2) OC=O	(CH_2) C	$(CH_3)_2$ C	$(CH_3)_X$ C
3c $C_{17}H_{26}O_8N_3P_3Cl_2$	34.35 34.11	4.47 4.35	6.97 7.02	4.67-4.11 (m,4H)	3.85-3.61 (3m,12H)	8.05-6.75 (2m,4H)		1.40-1.30 (t,3H)	4.36-4.29 (qt,2H)	1.69-1.66 (2s,2H)	1.31-1.23 (2s,6H)	0.68 (s,9H)
3d $C_{22}H_{38}O_6N_3P_3Cl_2$	41.30 41.38	5.88 5.96	6.64 6,58	4.45-4.08 (m,4H)	3.85-3.57 (2m,12H)	7.31-6.71 (3m,4H)						
3e $C_{15}H_{21}O_7N_3P_3Cl_2$	32.55 32.46	3.83 3.79	7.48 7.57	4.58-4.15 (2m,2H)	3.91-3.44 (m,12H)	7.95 6.93 (4m,4H)	10.50-10.40 (S,1H)					
3f $C_{15}H_{21}O_7N_3P_3Cl_2$	32.60 32.46	3.88 3.79	7.49 7.57	4.58-4.09 (2m,4H)	4.00-3.53 (m,12H)	8.09-7.16 (2m,4H)	10.02 9.90 (2s,1H)					

[a]Calcd./found. [b]In $CDCl_3$

Table S3 ^{31}P NMR data for tetraaryloxy-substituted PNP-lariat ethers **4c-f**.

	^{31}P{-1H} NMR, A_2B spin system[a]		
	δ_P, ppm		
Compound	P_A[c]	P_B[d]	J_{P-P}, Hz[b]
4c	12.80 (d)	8.90 (t)	93.5
4d	13.70 (d)	9.40 (t)	89.6
4e	13.70 (d)	9.67 (t)	91.0
4f	13.47 (d)	9.71 (t)	91.2

[a]A_2B spin system: P_A = P(OCH_2~)[OAr]; P_B = PCl_2; d - double doublet, corresponds to P_A (2 equally substituted P atoms), t - triplet, corresponds to P_{B-} P_A [b]J_{P-P} and $\delta_P$values calculated according to ref. 28. [c]Proton coupling causes collapse into a broad doublet. [d]Proton coupling causes weak broadening.

Table S4 Combustion analysis and ^{1}H NMR spectral data for tetraaryloxy-substituted PNP-lariat ethers **4c-f**.

Formula	Elemental analysis, %[a] C	H	N	^{1}H NMR δ_H, ppm[b] (CH_2) OP	(CH_2) OC	$(CH)_{Ar}$	CHO	CH_3	(CH_2) OC=O
4c $C_{44}H_{60}O_9N_3P_3$	53.30 53.44	5.98 6.07	4.33 4.25	4.39- 4.05 (m,4H)	3.71- 3.58 (2m,12H)	7.83- 6.81 (4m,16H)		1.39- 1.28 (t,12H)	4.37- 4.29 (qt,8H)
4d $C_{50}H_{104}O_9N_3P_3$	52.41 52.26	9.20 9.06	3.57 3.66	4.90- 4.15 (m,4H)	3.75- 3.61 (2m,12H)	7.94- 6.84 (2m,16H)		1.39- 1.32 (t,12H)	4.36- 4.28 (qt,8H)
4e $C_{36}H_{36}O_{13}N_3P_3$	53.09 53.27	4.32 4.44	5.30 5.18	4.40- 4.00 (2m,4H)	3.89- 3.52 (2m,12H)	8.00- 6.94 (5m,16H)	10.40- 9.89 (3s,4H)		
4f $C_{36}H_{36}O_{13}N_3P_3$	53.13 53.27	4.40 4.44	5.24 5.18	4.27- 4.07 (m,4H)	3.80- 3.57 (2m,12H)	8.00- 7.03 (6M,16H)	10.04 9.83 (2s,4H)		

[a]-Calcd./found. [b]In $CDCl_3$

Table S5 ^{31}P NMR spectral data for per-(2-naphthyloxy) *gem*-polymethylenediamino-bridged PNP-bis-lariat ethers **10a-f** and monomeric PNP-lariat ether analogue **7**.

		$^{31}P\{-^{1}H\}$ NMR, AMX spin system						$^{31}P\{^{1}H\}$ NMR		
		δ_P, ppm[b]			J_{P-P}, Hz[c]			J_{P-H}, Hz		
Compound	n[a]	P_A	P_M	P_X	A-M	A-X	M-X	P_AH[e]	P_MH[f]	P_X-H[g]
7	3	16.87	9.24	26.36	71.9	66.6	58.1	8.5	7.2	
10a	2	14.28	10.75	21.38	72.6	72.2	85.3	8.2	7.3	
10b	3	14.45	10.96	21.49	71.8	71.8	85.2	9.4	7.1	
10c	6	14.57	11.10	21.65	71.5	71.7	85.9	8.4	7.4	
10d	7	14.54	11.06	21.60	71.5	71.5	85.9	8.7	7.5	
10e	10	14.64	11.18	21.61	71.4	71.4	85.9	8.9	7.3	
10f	12	14.63	11.16	21.60	71.4	71.4	85.9	8.5	7.3	

[a]Number of CH_2 groups in the oligomethylene(di)amino substituent [b]δ_P and J_{P-P} values for the AMX coupling system were calculated according to ref. 27. For **7**: P_A = P(OCH_2~)(NHPr): P_M = P(OCH_2~)(ONaph) P_X = P(ONaph)$_2$. For **10a-f**: P_A = P(OCH_2~)(NHR); P_M =; P(OCH_2~)(ONaph) P_X = P(ONaph)$_2$ [c]Degenerate double doublet (collapse into a triplet due to overlap of the inner lines. [d]Well-resolved double doublets. [e]Each line splits into 6 signals on proton coupling. [f]Each line splits into a triplet. [g]Lack of noticeable proton coupling.

Table S6 Combustion analysis and ^{1}H NMR spectral data for heterogeneously disubstituted PNP-lariat ether **7** and bis-PNP-lariat ethers **10a-f**.

Formula	Elemental analysis, %[a] C	H	N	^{1}H NMR δ_H, ppm[b] (CH_2) OP	(CH_2) OC	$(CH)_{Ar}$	NH	CH_2N	CH_3	CH_3
7 $C_{21}H_{31}O_6N_4P_3Cl_2$	42.15 42.07	5.28 5.17	9.28 9.35	4.60-4.40 (m,4H)	4.40-3.45 (3m,12H)	7.88-7.45 (3m,7H)	1.87-1.67 (2m,1H)	3.00-2.80 (m,2H)	0.99-0.77 (m,3H)	1.44-1.19 (2m,2H)
10a $C_{78}H_{80}O_{16}N_8P_6$	59.73 59.62	5.18 5.10	7.00 7.13	4.60-4.40 (m,4H)	4.40-3.45 (3m,12H)	7.88-7.45 (3m,7H)		2.50-2.10 (m,4H)		
10b $C_{79}H_{82}O_{16}N_8P_6$	59.99 59.85	5.27 5.18	7.01 7.07	4.34-4.10 (2m,8H)	3.71-3.36 (m,24H)	7.82-7.12 (m,42H)		2.18 (d,4H)		0.67 (s,2H)
10c $C_{82}H_{88}O_{16}N_8P_6$	60.47 60.52	5.36 5.41	6.92 6.89	4.65-4.20 (2m,8H)	3.83-3.39 (m,24H)	7.89-7.20 (m,42H)		2.45-2.00 (m,4H)		0.60 (m,8H)
10d $C_{83}H_{90}O_{16}N_8P_6$	60.85 60.73	5.61 5.49	6.72 6.83	4.20-3.78 (2m,8H)	3.67-3.37 (m,24H)	7.89-7.20 (m,42H)		2.31-1.96 (2m,4H)		0.83-0.54 (2m,10H)
10e $C_{86}H_{96}O_{16}N_8P_6$	61.44 61.36	5.83 5.71	6.60 6.66	4.75-4.22 (2m,8H)	3.52-3.47 (m,24H)	7.80-7.23 (m,42H)		2.40-1.83 (m,4H)		0.93 (m,8H)
10f $C_{88}H_{100}O_{16}N_8P_6$	61.90 61.75	5.93 5.85	6.49 6.55	4.16-3.81 (2m,8H)	3.65-3.34 (m,24H)	7.87-7.18 (m,42H)		2.31-2.33 (m,4H)		0.76-1.26 (m,10H)

[a]Calcd./found. [b]In $CDCl_3$.