Electronic Supplementary Information

Liquid membrane transport of potassium fluoride by the organotin-based ditopic host Ph₂FSnCH₂SnFPh-CH₂-[19]-crown-6

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Table of Contents

1. Scheme S1. Synthesis of Organotin-based Receptor 1	2
2. General information	2
3. Synthetic procedures and characterization data for compounds 1 and 1.KF	3
4. Figure S1. Schematic drawing of the apparatus used for the transport experiments	5
5. Figure S2. Showing ditopic complexation of 1 with KF	5
6. Table S1: Electrical conductivity data showing transport activity of the ditopic	
receptor 1 for 0.37 M salt concentration in the source phase	6
7. Table S2: Electrical conductivity data showing transport activity of the ditopic	
receptor 1 for 8.0 M salt concentration in the source phase	8
8. Figure S3. Plot of the electric conductivity vs time when the monotopic	
receptor 2 or 3 were independently used as transporter	10
9. Figure S4. Plot of the electric conductivity vs time for a blank experiment	
where no receptor had been dissolved in the organic layer.	11
10. Copies of spectra	12



Scheme S1. Synthesis of organotin-based receptor 1

General Information

NMR Spectroscopy. NMR spectra were recorded on DRX 400, DPX 300, Varian Nova 600 spectrometers with broad band decoupling of ¹¹⁹Sn at 111.92 MHz, ¹⁹F at 282.4 MHz, ¹³C at 100.61 MHz and ¹H at 300 or 400 MHz. Chemical shifts δ are given in ppm and referenced to tetramethylstannane (¹¹⁹Sn), CFCl₃ (¹⁹F), and the deuterated solvent (¹H, ¹³C). The following abbreviations are used for signals assignments: br (broad), brs (broad singlet), s (singlet), d (doublet), dd (doublet), q (quadruplet), m (multiplet), brm (broad multiplet).

Complexation Studies. The samples for NMR analyses were prepared by dissolving ca. 50 mg of compound **1** and four equiv. KF in CD₃CN. Potassium fluoride used for the complexation studies were dried in vacuo (10^{-6} mbar) at 100° C for one day and stored under nitrogen.

Electrospray mass spectra were recorded on a Thermoquest-Finnigan instrument using CH₃CN as the mobile phase. The samples were introduced as solution in CH₃CN via a syringe pump operating at 0.5 μ L/min. The capillary voltage was 4.5 kV while the cone skimmer voltage varied between 50 and 250 kV. Identification of the expected ions was assisted by comparison of experimental and calculated isotope distribution patterns. The m/z values reported correspond to those of the most intense peak in the corresponding isotope pattern.

Transport experiments. The conductivity was determined with an apparatus of the type LF530 from the company Wissenschaftlich-Technische Werkstätten. The cell was calibrated at 25°C with a KCl standard solution.

Synthesis of ditopic receptor A.

The ditopic receptor **A** in Scheme S1 was prepared according to our previously reported procedure [Organometallics **2008**, *27*, 5577-5587].

Synthesis of ditopic receptor 1.

A solution of $18-(\{iodophenyl[(iododiphenylphenylstannyl)methyl]-stannyl\}methyl)-$ 1,4,7,10,13,16-hexaoxanonadecane **A** (0.5 g, 0.478 mmol) in CH₂Cl₂ (20 mL) was mixed with a solution of KF (0.85 g, 14.631 mmol) in water (25 mL). The biphasic mixture was stirred at room temperature for ten days. The organic phase was then separated and dried over MgSO₄. Removal of the solvent in vacuo afforded 0.31 g (80%) of pure **1** as white solid.

18-({fluorophenyl[(fluorodiphenylstannyl)methyl]-stannyl}methyl)-1,4,7,10,13,16-

hexaoxanonadecane (**1**): m. p. 130 °C. ¹H-NMR (CDCl₃, 300.13 MHz, 293K) δ: 1.13 (br, 2H, SnCH₂), 2.24 (br, 2H, SnCH₂-Sn), 3.13 (br, 1H, CH), 3.52-3.62 (24H, CH₂-O-CH₂), 7.31-7.79

(brm, 15H, Ph). ¹³C{¹H}-NMR (CDCl₃, 100.63 MHz, 293K) δ : 16.1 (Sn-CH₂.Sn), 30.0 (Sn-CH₂), 36.9 (CH), 74.5 (O-CH₂.CH), 77.3 (complex broad, CH₂-O-CH₂), 128.6-143.6 (*o*,*m*,*p*-Ph). ¹⁹F{¹H}-NMR (CDCl₃, 282.4 MHz) at 293 K, δ -176.2 (br); at 233 K, δ -173.2 (¹*J*(¹⁹F-¹¹⁷Sn) = 2045 Hz, ¹*J*(¹⁹F-¹¹⁹Sn) = 2127 Hz, ³*J*(¹⁹F-^{117/119}Sn) = 236 Hz, SnFPh₂ and SnFPh). Elemental Anal. for C₃₃H₄₄ F₂O₆Sn₂·2H₂O (848.16), Cacld : C 46.7, H 5.7; Found: C 46.5, H 5.3.

1·KF. Potassium fluoride, KF, (14.1 mg, 0.242 mmol) was added to a solution of **1** (50.0 mg, 0.061 mmol) in CD₃CN. ¹H-NMR (CD₃CN, 400.13 MHz, 293K) δ : 1.00 (d, ³*J*(¹H-¹H) = 6.8 Hz, ²*J*(¹H-¹¹⁷Sn) =67.6 Hz, ²*J*(¹H-¹¹⁹Sn) =76.8 Hz, 2H SnC*H*2), 1.22 (s, ²*J*(¹H-^{117/119}Sn) = 76.8 Hz, SnC*H*2-Sn), 2.22 (m, 1H, C*H*), 3.29-3.54 (complex pattern, 24H, C*H*₂-O-C*H*₂), 7.27-7.33 (m, 8H, Ph), 7.61 (m, 2H, Ph), 7.77-7.94 (m, *J*_{H,Sn} = 56.0/67.6 Hz, 5H, Ph). ¹³C{¹H}-NMR (CDCl₃, 100.63 MHz, 293K) δ : 5.8 (q, ²*J*(¹³C-¹⁹F) = 26.3 Hz, Sn-CH₂-Sn), 20.2 (d, ²*J*(¹³C-¹⁹F) = 8.7 Hz, Sn-CH₂), 37.1 (*C*H), 70.6-71.5 (complex pattern, CH₂-O-CH₂), 75.9 and 79.2 (³*J*(¹³C-^{117/119}Sn = 65.1 Hz, CH-CH₂-O), 128.3-146.7 (*o*,*m*,*p*-Ph). ¹⁹F{¹H}-NMR (CD₃CN, 282.4 MHz) at 296 K δ : -164.9 (br, v_{1/2} = 6908 Hz); at 233 K δ : -90.3 (br, v_{1/2} = 1891 Hz, Sn-F–Sn), -163.5 (brs, v_{1/2} = 707 Hz, ¹*J*(¹⁹F-^{117/119}Sn) = 2056 Hz, SnFPh₂ or SnFPh), -167.4 (br, v_{1/2} = 978 Hz, ¹*J*(¹⁹F-^{117/119}Sn) = 2253 Hz, SnFPh₂ or SnFPh). ¹¹⁹Sn{¹H}-NMR (CD₃CN, 111.93 MHz) at 296 K δ : -116.3 (br, v_{1/2} = 2684 Hz), -194.2 (br, v_{1/2} = 1814 Hz); at 233 K δ : -112.2 (dd, ¹*J*(¹¹⁹Sn-¹⁹F₁) = 2132.7 Hz, ¹*J*(¹¹⁹Sn-¹⁹F_b) = 596.6 Hz, SnF₂Ph₂), -191.6 (dd, ¹*J*(¹¹⁹Sn-¹⁹F₁) = 3119.9 Hz, ¹*J*(¹¹⁹Sn-¹⁹F_b) = 150.1 Hz, SnF₂Ph).



Figure S1. Schematic drawing of the apparatus used for the transport experiments



Figure S2. Showing ditopic complexation of KF by host 1.

Receptor (R ₁): 1							
C_{R1} = 0.03 M , C_{KF} = 0.37 M; V_{sol} = 6 mL							
t/h	cond (µS/cm)	t/h	cond (µS/cm)	t/h	cond		
					(µS/cm)		
0	23.1	148	1406	265	2290		
63	701	159.5	1496	280	2420		
75.5	794	169	1572	288.5	2490		
88	912	186.5	1688	304.5	2580		
95.5	993	231	2030	312	2620		
111.5	1135	240.5	2160	375.5	3330		
120.5	1205	255.5	2240	386	3450		
135	1316						
	Receptors: 18	3-crown-6 (R ₂) 2,	Ph ₂ FSnCH ₂ SnF	Ph ₂ (R ₃) 3 ,			
(18-crown-6 + Ph ₂ FSnCH ₂ SnFPh ₂) (R ₂ + R ₃) (2 + 3)							
	$C_{R2} = C_{I}$	$_{R3} = 0.03 \text{ M}$, C_{KF}	= 0.37 M; V _{sol} =	6 mL			
	2		3	Dual hos	t 2 + 3		
t/h	cond (µS/cm)	t/h	cond (µS/cm)	t/h	cond		
					(µS/cm)		
0	14.2	0	17.5	0	19		
63	35.1	63	22.1	63	204		
75.5	44.1	75.5	30.2	75.5	280		
88	51.9	88	34.1	88	301		
95.5	52	95.5	65.5	95.5	313		
111.5	52	111.5	102	111.5	332		
120.5	51.3	120.5	120	120.5	343		
135	51	135	150	135	358		
148	50	148	160	148	371		
159.5	50	159.5	170	159.5	387		
169	50	169	180	169	399		
186.5	50	186.5	200	186.5	426		
231	50	231	210	231	467		

Table S1: Electrical conductivity data showing transport activity of the ditopic receptor 1 for0.37 M salt concentration in the source phase

240.550240.5220240.5255.540255.5230255.5	479 490
255.5 40 255.5 230 255.5	490
265 40 265 250 265	498
280 40 280 320 280	515
288.5 40 288.5 240 288.5	528
304.5 40 304.5 380 304.5	543
312 40 312 390 312	550
375.5 40 375.5 400 375.5	608
386 40 386 410 386	620

Receptors (R ₁): 1							
C_{R1} = 0.03 M , C_{KF} = 8.0 M; V_{sol} = 6 mL							
t/h	cond (µS/cm) t/h		cond (µS/cm)	t/h	cond		
					(µS/cm)		
0	31.5	97.5	2150	223	4350		
22	322	103.5	2270	239	4540		
33	1125	120	2500	249	4640		
47	1486	128.5	2620	291	5260		
55.5	1639	143.5	2830	198	5340		
71.5	1814	152	2940	310.5	5430		
79.5	1921	216	4180	322	5510		
	Receptors: 1	8-crown-6 (R ₂) 2	Ph ₂ FSnCH ₂ SnF	Ph ₂ (R ₃) 3 ,	<u>I</u>		
	(18-crown-	6 + Ph ₂ FSnCH ₂	$SnFPh_2$) ($R_2 + R_3$	₃) (2 + 3)			
	$C_{R2} = C$	$C_{R3} = 0.03 \text{ M}$, C_{K}	$_{\rm F}$ = 8.0 M; V _{sol} =	6 mL			
	2		3	Dual hos	st 2 + 3		
t/h	cond (µS/cm)	t/h	cond (µS/cm)	t/h	cond		
					(uS/cm)		
0					(μο/οπ)		
v	14.2	0	18.5	0	14.3		
7	14.2 44.1	0 22	18.5 25.1	0 22	14.3 120.7		
7 21	14.2 44.1 51.9	0 22 33	18.5 25.1 32.3	0 22 33	14.3 120.7 408		
7 21 27	14.2 44.1 51.9 52	0 22 33 47	18.5 25.1 32.3 37.8	0 22 33 47	14.3 120.7 408 541		
7 21 27 56	14.2 44.1 51.9 52 52	0 22 33 47 55.5	18.5 25.1 32.3 37.8 69.4	0 22 33 47 55.5	14.3 120.7 408 541 613		
7 21 27 56 73	14.2 44.1 51.9 52 52 51.3	0 22 33 47 55.5 71.5	18.5 25.1 32.3 37.8 69.4 108	0 22 33 47 55.5 71.5	14.3 120.7 408 541 613 717		
7 21 27 56 73 101.5	14.2 44.1 51.9 52 52 51.3 51	0 22 33 47 55.5 71.5 79.5	18.5 25.1 32.3 37.8 69.4 108 140	0 22 33 47 55.5 71.5 79.5	14.3 120.7 408 541 613 717 769		
7 21 27 56 73 101.5 118	14.2 44.1 51.9 52 52 51.3 51 50	0 22 33 47 55.5 71.5 79.5 97.5	18.5 25.1 32.3 37.8 69.4 108 140 170	0 22 33 47 55.5 71.5 79.5 97.5	14.3 120.7 408 541 613 717 769 850		
7 21 27 56 73 101.5 118 126	14.2 44.1 51.9 52 52 51.3 51 50 50	0 22 33 47 55.5 71.5 79.5 97.5 103.5	18.5 25.1 32.3 37.8 69.4 108 140 170 180	0 22 33 47 55.5 71.5 79.5 97.5 103.5	14.3 120.7 408 541 613 717 769 850 890		
7 21 27 56 73 101.5 118 126 142	14.2 44.1 51.9 52 52 51.3 51 50 50 50	0 22 33 47 55.5 71.5 79.5 97.5 103.5 120	18.5 25.1 32.3 37.8 69.4 108 140 170 180 190	0 22 33 47 55.5 71.5 79.5 97.5 103.5 120	14.3 120.7 408 541 613 717 769 850 890 980		
7 21 27 56 73 101.5 118 126 142 149.5	14.2 44.1 51.9 52 52 51.3 51 50 50 50 50	0 22 33 47 55.5 71.5 79.5 97.5 103.5 120 128.5	18.5 25.1 32.3 37.8 69.4 108 140 170 180 190 200	0 22 33 47 55.5 71.5 79.5 97.5 103.5 120 128.5	14.3 120.7 408 541 613 717 769 850 890 980 1050		
7 21 27 56 73 101.5 118 126 142 149.5 166	14.2 44.1 51.9 52 52 51.3 51 50 50 50 50 50 50	0 22 33 47 55.5 71.5 79.5 97.5 103.5 120 128.5 143.5	18.5 25.1 32.3 37.8 69.4 108 140 170 180 190 200 210	0 22 33 47 55.5 71.5 79.5 97.5 103.5 120 128.5 143.5	14.3 120.7 408 541 613 717 769 850 890 980 1050 1130		
7 21 27 56 73 101.5 118 126 142 149.5 166 174	14.2 44.1 51.9 52 52 51.3 51 50 50 50 50 50 50 50 50 50	0 22 33 47 55.5 71.5 79.5 97.5 103.5 120 128.5 143.5 152	18.5 25.1 32.3 37.8 69.4 108 140 170 180 190 200 210 220	0 22 33 47 55.5 71.5 79.5 97.5 103.5 120 128.5 143.5 152	14.3 120.7 408 541 613 717 769 850 890 980 1050 1130 1180		

 Table S2: Electrical conductivity data showing transport activity of the ditopic receptor 1 for 8.0 M salt concentration in the source phase

199.5402232402231610215.5402392502391670286.5402493202491740295.5402912402912010310.5401983801982050318.540310.5390310.52090335403224003222130341						
215.5402392502391670286.5402493202491740295.54029120102010310.5401983801982050318.540310.5390310.52090335403224003222130341420	199.5	40	223	240	223	1610
286.5402493202491740295.54029120102010310.5401983801982050318.540310.5390310.52090335403224003222130341420	215.5	40	239	250	239	1670
295.5402912402912010310.5401983801982050318.540310.5390310.52090335403224003222130341410359.5420	286.5	40	249	320	249	1740
310.5401983801982050318.540310.5390310.52090335403224003222130341410359.5-420	295.5	40	291	240	291	2010
318.540310.5390310.52090335403224003222130341410359.5-420	310.5	40	198	380	198	2050
335403224003222130341410410420	318.5	40	310.5	390	310.5	2090
341 410 359.5 420	335	40	322	400	322	2130
359.5 420	341			410		
	359.5			420		



Figure S3. Plot of the electric conductivity vs time when the monotopic receptor 2 (top) or 3 (bottom) were independently used as transporter



Figure S4. Plot of the electric conductivity vs time for a blank experiment where no receptor had been dissolved in the organic layer.

Copies of NMR spectra

¹H NMR spectrum of the ditopic receptor 1



(**300MHz, CDCl₃, RT**)

¹³C NMR spectrum of the ditopic receptor 1

(CDCl₃, RT)

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120 100 80 60 40

Chemical Shift (ppm)

20 0

160

140

¹⁹F NMR spectrum of the ditopic receptor 1



¹⁹F NMR spectrum of the ditopic receptor 1

(CDCl₃, -40°C)



¹H NMR spectrum of 1·KF

(400 MHz, CD₃CN, room temperature)



¹³C NMR spectrum of 1·KF

(CD	CN	RT)
(UD)	$\langle \mathbf{C} \mathbf{I} \mathbf{V} \rangle$	111

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¹³C NMR spectrum of 1·KF (cutout)



¹³C NMR spectrum of 1·KF (cutout)

(CD₃CN, RT)

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¹³C NMR spectrum of 1·KF (cutout)



¹¹⁹Sn NMR spectrum of 1·KF



¹¹⁹Sn NMR spectrum of 1·KF

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(CD<sub>3</sub>CN, -40°C)
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¹⁹F NMR spectrum of 1·KF

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¹⁹F NMR spectrum of 1·KF

(CD₃CN, -40°C)

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