

Novel Ditopic 2-Mercaptothiazoles and their Sodium Salts: Synthesis, Structural Diversity and Luminescence

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Table 1S. Details of crystallographic, collection and refinement data for **1**, Na₂dmbt(DME)₄, Na₂L²(DME)₄, Na₂L⁵(DME)₄, [Na₂L⁴(THF)₄]_n and [Na₂L⁴(DME)₂]_n.

Complex	1	Na ₂ dmbt(DME) ₄	Na ₂ L ² (DME) ₄	Na ₂ L ⁵ (DME) ₄	[Na ₂ L ⁴ (THF) ₄] _n	[Na ₂ L ⁴ (DME) ₂] _n
Empirical formula	C ₁₂ H ₁₂ F ₂ N ₂ O ₂ S ₄	C ₂₄ H ₄₂ N ₂ Na ₂ O ₈ S ₄	C ₂₄ H ₄₀ F ₂ N ₂ Na ₂ O ₈ S ₄	C ₂₈ H ₄₄ N ₂ Na ₂ O ₈ S ₄	C ₂₄ H ₃₄ N ₂ Na ₂ O ₄ S ₄	C ₁₆ H ₂₂ N ₂ Na ₂ O ₄ S ₄
Formula weight	382.48	660.81	696.80	710.87	588.75	480.57
Temperature [K]	100(2)	100(2)	100(2)	200(2)	100(2)	100(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Monoclinic
Space group	P-1	P2 ₁ /n	P2 ₁ /n	P-1	Pbca	P2 ₁ /c
Unit cell dimensions						
a[Å]	8.2628(6)	17.2189(7)	17.3479(6)	8.7022(4)	15.2774(6)	7.6815(3)
b[Å]	9.9330(5)	9.9368(4)	10.1004(3)	8.8311(4)	11.0794(4)	13.6933(5)
c[Å]	10.3705(6)	20.0201(8)	19.6252(6)	12.7825(6)	16.7363(7)	10.3983(4)
α[°]	93.322(5)	90	90	79.4431(15)	90	90
β[°]	107.069(6)	99.5650(10)	98.0100(10)	84.4180(15)	90	101.9643(11)
γ[°]	103.852(5)	90	90	77.5543(15)	90	90
Volume [Å ³]	782.42(9)	3377.8(2)	3405.19(19)	941.30(8)	2832.86(19)	1069.99(7)
Z	2	4	4	1	4	2
Calculated density [Mg/m ³]	1.623	1.299	1.359	1.254	1.380	1.492
Absorption coefficient [mm ⁻¹]	0.634	0.351	0.360	0.320	0.399	0.510
F(000)	392	1400	1464	376	1240	500
Crystal size [mm ³]	0.40×0.10×0.05	0.12×0.09×0.08	0.35×0.23×0.17	0.29×0.23×0.07	0.21×0.17×0.08	0.28×0.17×0.08
θ [°]	3.174 – 26.999	2.063 – 27.134	2.096 – 29.575	2.401 – 28.695	2.576 – 30.117	2.494 – 28.698
Reflections collected / unique	6815 / 3414	42795 / 7473	51628 / 9531	13963 / 4836	46605 / 4153	16878 / 2767
R(int)	0.0299	0.0415	0.0357	0.0281	0.0395	0.0314
Final R indices [I>2σ(I)]	R ₁ =0.0352, wR ₂ =0.0844	R ₁ =0.0337, wR ₂ =0.0694	R ₁ =0.0329, wR ₂ =0.0684	R ₁ =0.0419, wR ₂ =0.0957	R ₁ =0.0308, wR ₂ =0.0724	R ₁ =0.0271, wR ₂ =0.0609
R indices (all data)	R ₁ =0.0475, wR ₂ =0.0891	R ₁ =0.0505, wR ₂ =0.0749	R ₁ =0.0483, wR ₂ =0.0745	R ₁ =0.0608, wR ₂ =0.1069	R ₁ =0.0437, wR ₂ =0.0777	R ₁ =0.0354, wR ₂ =0.0640
S	1.035	1.025	1.013	1.030	1.027	1.071
Largest diff. peak and hole [e/Å ³]	0.694/-0.326	0.289/-0.254	0.404/-0.298	0.249/-0.289	0.421/-0.300	0.435/-0.271

Table 2S. The selected bond lengths (Å) and angles (°) in the compounds **1**, Na₂dmbt(DME)₄, Na₂L²(DME)₄, Na₂L⁵(DME)₄, [Na₂L⁴(THF)₄]_n and [Na₂L⁴(DME)₂]_n.

Bonds, Å	1	Na ₂ dmbt(DME) ₄	Na ₂ L ² (DME) ₄	Na ₂ L ⁵ (DME) ₄	[Na ₂ L ⁴ (THF) ₄] _n	[Na ₂ L ⁴ (DME) ₂] _n
Na(1)-S(1)	-	2.9475(7)	3.0830(6)	2.8877(8)	2.9686(6)	2.8478(3)
Na(1)-S(1)-S1*	-	-	-	-	2.8428(6)	-
Na(2)-S(1)	-	-	-	-	-	2.8999(3)
Na(2)-S(4)	-	2.8855(7)	2.9149(6)	-	-	-
Na(1)-N(1)	-	2.4145(14)	2.3968(12)	2.4316(15)	2.4026(11)	2.5637(11)
Na(2)-N(2)	-	2.4072(14)	2.4022(12)	-	-	-
Na...Na	-	-	-	-	5.7382(7)	3.84075(15)
Na-O _{sol}	-	2.3317(12) - 2.4470(12)	2.3176(10) - 2.4422(11)	2.352(14) - 2.50(3)	2.24(2) - 2.332(14)	2.3832(9) - 2.4865(9)
S(1)-C(1)	1.646(2)	1.6975(16)	1.6919(13)	1.7024(17)	1.7131(12)	1.7200(13)
S(2)-C(2)	1.743(2)	1.7452(16)	1.7370(13)	1.7386(16)	1.7436(12)	1.7428(13)
S(2)-C(1)	1.765(2)	1.7843(15)	1.7886(13)	1.7703(17)	1.7755(12)	1.7614(13)
S(3)-C(6)	1.742(2)	1.7435(16)	1.7383(13)	-	-	-
S(3)-C(8)	1.756(2)	1.7866(16)	1.7881(13)	-	-	-
S(4)-C(8)	1.651(2)	1.6994(16)	1.6952(14)	-	-	-
N(1)-C(1)	1.354(3)	1.3175(19)	1.3203(16)	1.322(2)	1.3127(15)	1.3145(16)
N(1)-C(3)	1.391(2)	1.3863(19)	1.3783(16)	1.3826(19)	1.3908(15)	1.3952(16)
N(2)-C(8)	1.354(3)	1.3154(19)	1.3206(16)	-	-	-
N(2)-C(7)	1.382(3)	1.3842(19)	1.3800(16)	-	-	-
F(1)-C(4)	1.347(2)	-	1.3594(14)	-	-	-
F(2)-C(5)	1.353(2)	-	1.3588(14)	-	-	-
Angles, °						
N(1)-Na(1)-S(1)	-	59.44(3)	57.22(3)	60.42(3)	58.97(3)	60.10(2)
N(1)-Na(1)-	-	-	-	-	91.32(3)	-

S(1)-S1*						
N(1)-Na(1)- N(1)-S2*	-	-	-	-	-	180.0
N(1)-Na(1)- S(1)-S2*	-	-	-	-	-	119.90(2)
S(1)-Na(1)- S(1)-S2*	-	-	-	-	-	180.0
N(2)-Na(2)- S(4)	-	60.55(3)	60.04(3)	-	-	-
S(1)-Na(2)- S(1)-S3*	-	-	-	-	-	180.0
Na(1)-S(1)- Na(1)-S4*	-	-	-	-	161.793(12)	-
Na(1)-S(1)- Na(2)	-	-	-	-	--	83.855(9)
Na(2)-O(1)- Na(1)	-	-	-	-	-	101.17(3)
C(1)-S(1)- Na(1)	-	73.19(5)	71.52(5)	74.53(6)	73.49(4)	76.37(4)
C(1)-S(1)- Na(2)	-	-	-	-	-	83.855(9)
C(8)-S(4)- Na(2)	-	73.56(5)	73.43(5)	-	-	-
C(1)-N(1)- Na(1)	-	100.05(9)	104.38(8)	98.54(10)	102.45(7)	93.90(8)
C(8)-N(2)- Na(2)	-	98.29(9)	99.41(8)	-	-	-
C(2)-S(2)- C(1)	91.68(10)	90.29(7)	90.01(6)	90.22(8)	90.03(5)	90.18(6)
C(6)-S(3)- C(8)	91.54(10)	90.32(7)	90.03(6)	-	-	-
S(1)-C(1)- S(2)	123.10(13)	120.26(9)	126.28(10)	120.35(10)	121.11(7)	118.14(7)
S(4)-C(8)- S(3)	123.71(12)	120.31(9)	126.39(10)	-	-	-
C(1)-N(1)- C(3)	115.65(18)	112.50(13)	112.06(11)	111.67(13)	111.93(10)	110.97(10)
C(8)-N(2)- C(7)	115.92(18)	112.71(13)	111.95(11)	-	-	-

* - Symmetry code: (\$1) $-x+1, y+1/2, -z+3/2$; (\$2) $-x, -y+1, -z+1$; (\$3) $-x+1, -y+1, -z+1$; (\$4) $-x+1, y-1/2, -z+3/2$.

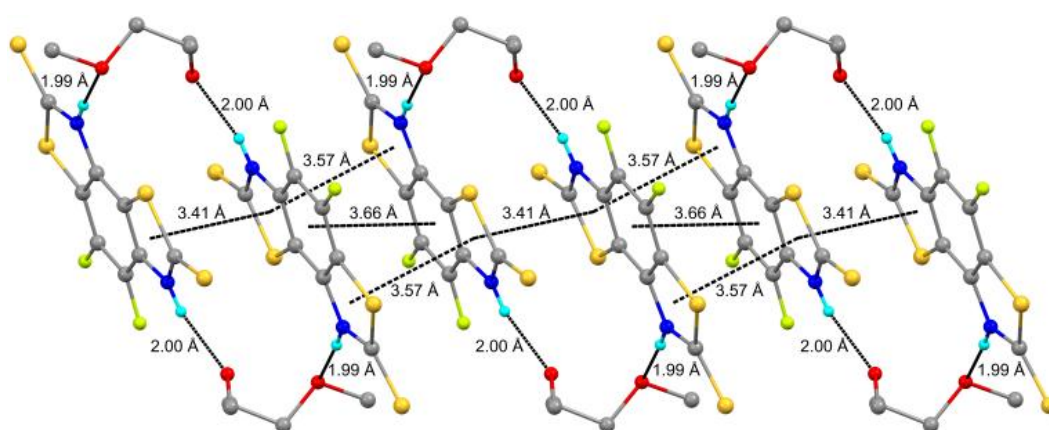


Figure 1S. Fragment of the crystal packing of **1**. The hydrogen atoms except H(1) and H(2) are omitted for clarity.

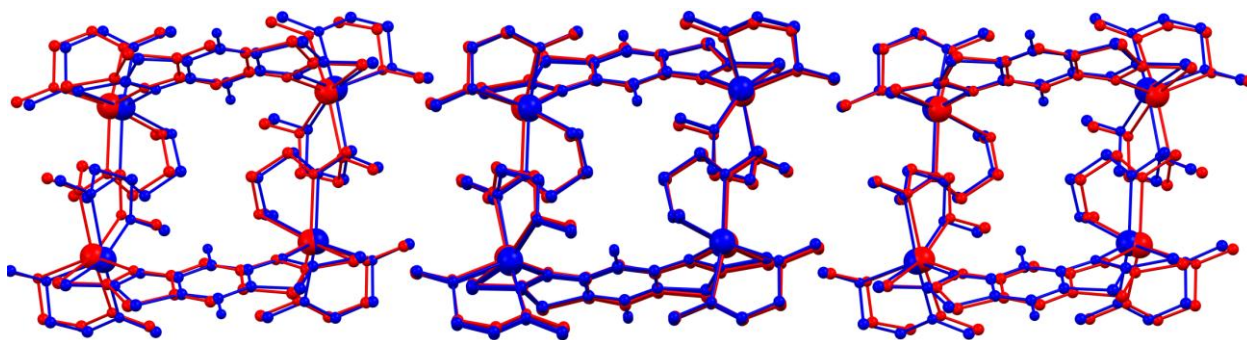


Figure 2S. The overlay of crystal packing of $\text{Na}_2\text{dmbt}(\text{DME})_4$ and $\text{Na}_2\text{L}^2(\text{DME})_4$ (blue).

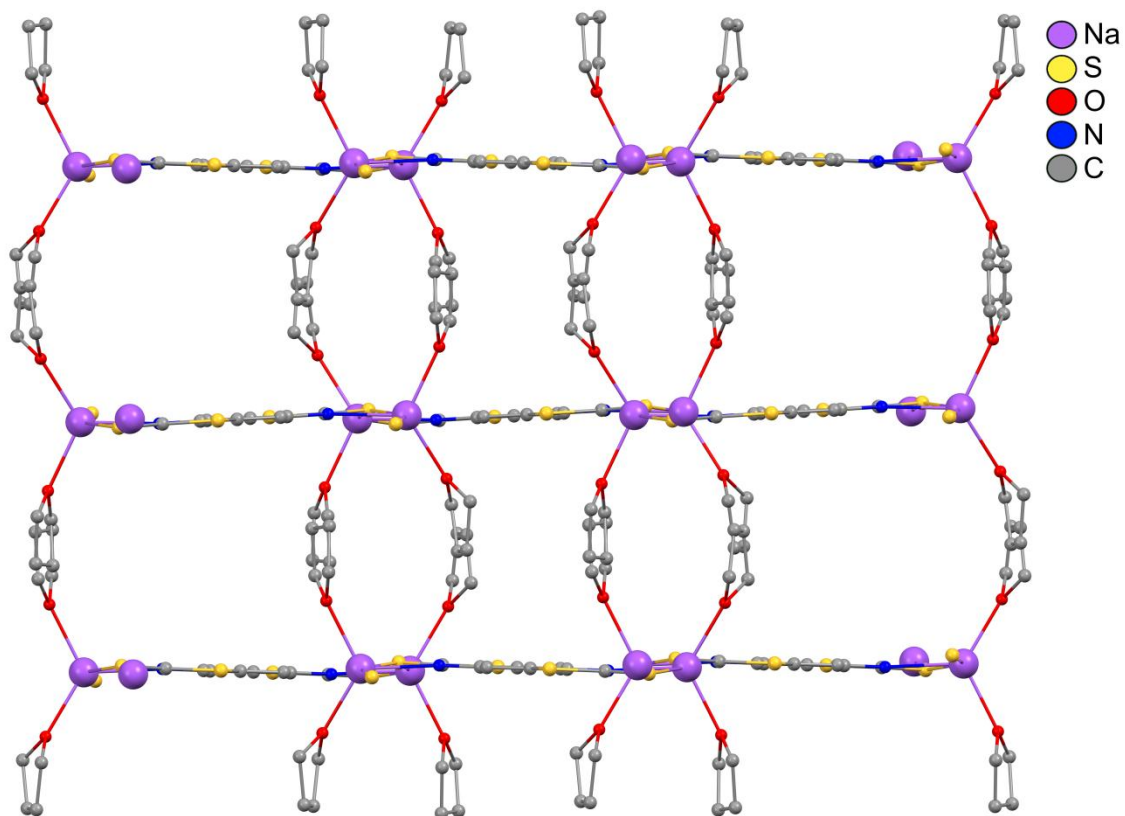


Figure 3S. Fragment of the crystal packing of $[\text{Na}_2\text{L}^4(\text{THF})_4]_n$. The hydrogen atoms are omitted for clarity.

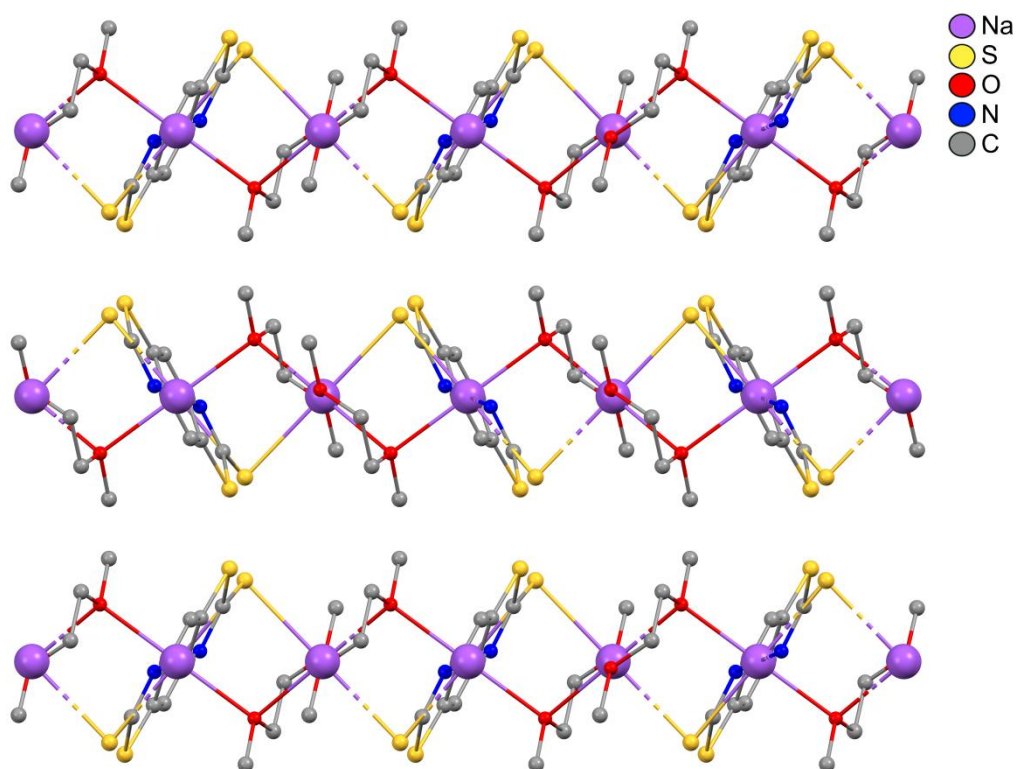


Figure 4S. Fragment of the crystal packing of $[\text{Na}_2\text{L}^4(\text{DME})_2]_n$. The hydrogen atoms are omitted for clarity.

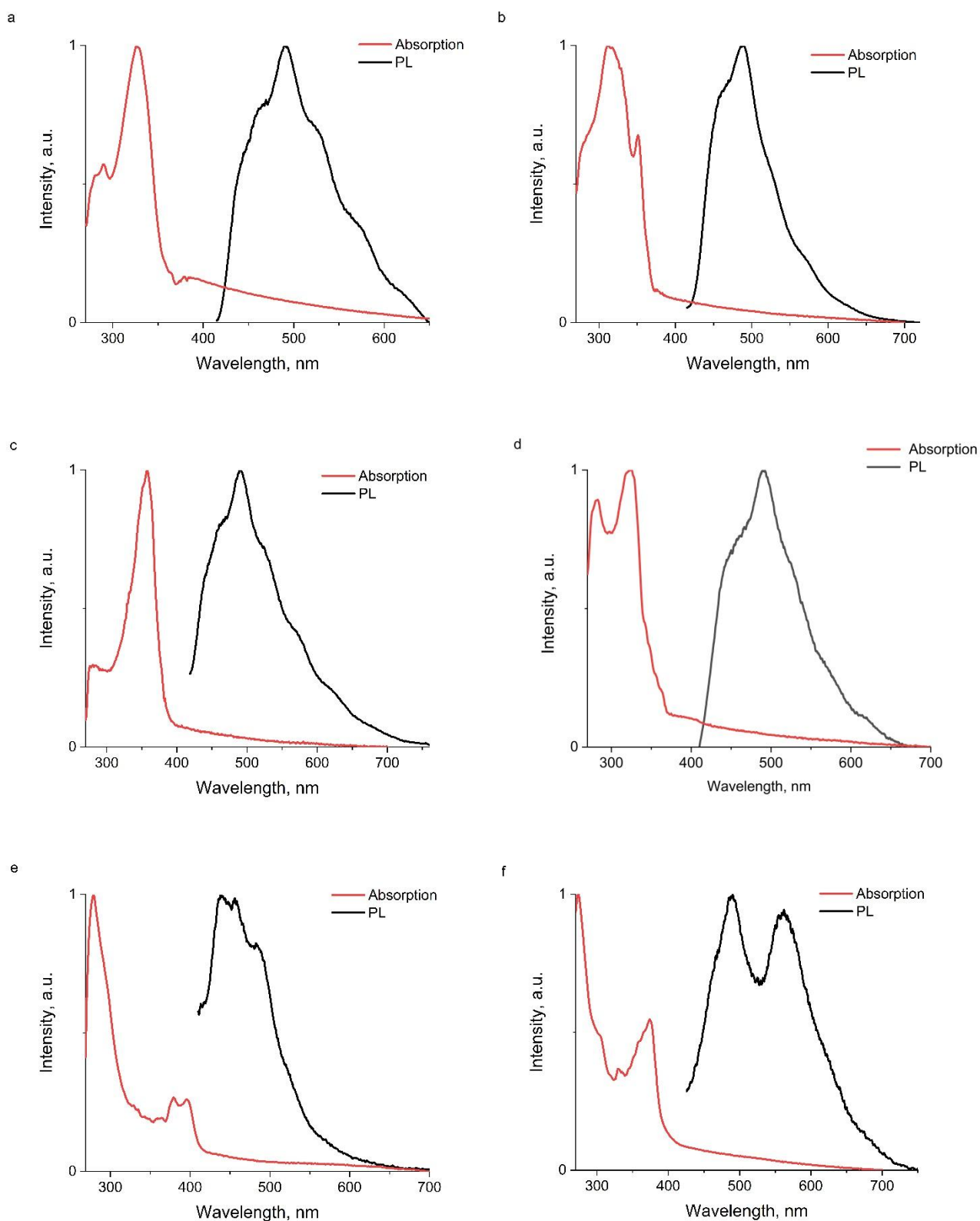


Figure 5S. Absorption and PL spectra of $\text{Na}_2\text{L}^1(\text{DME})_4$ (a), $\text{Na}_2\text{L}^2(\text{DME})_4$ (b), $\text{Na}_2\text{L}^3(\text{DME})_4$ (c), $[\text{Na}_2\text{L}^4(\text{DME})_2]_n$ (d), $\text{Na}_2\text{L}^5(\text{DME})_4$ (e), $\text{Na}_2\text{dmbt}(\text{DME})_4$ (f) at 298 K.

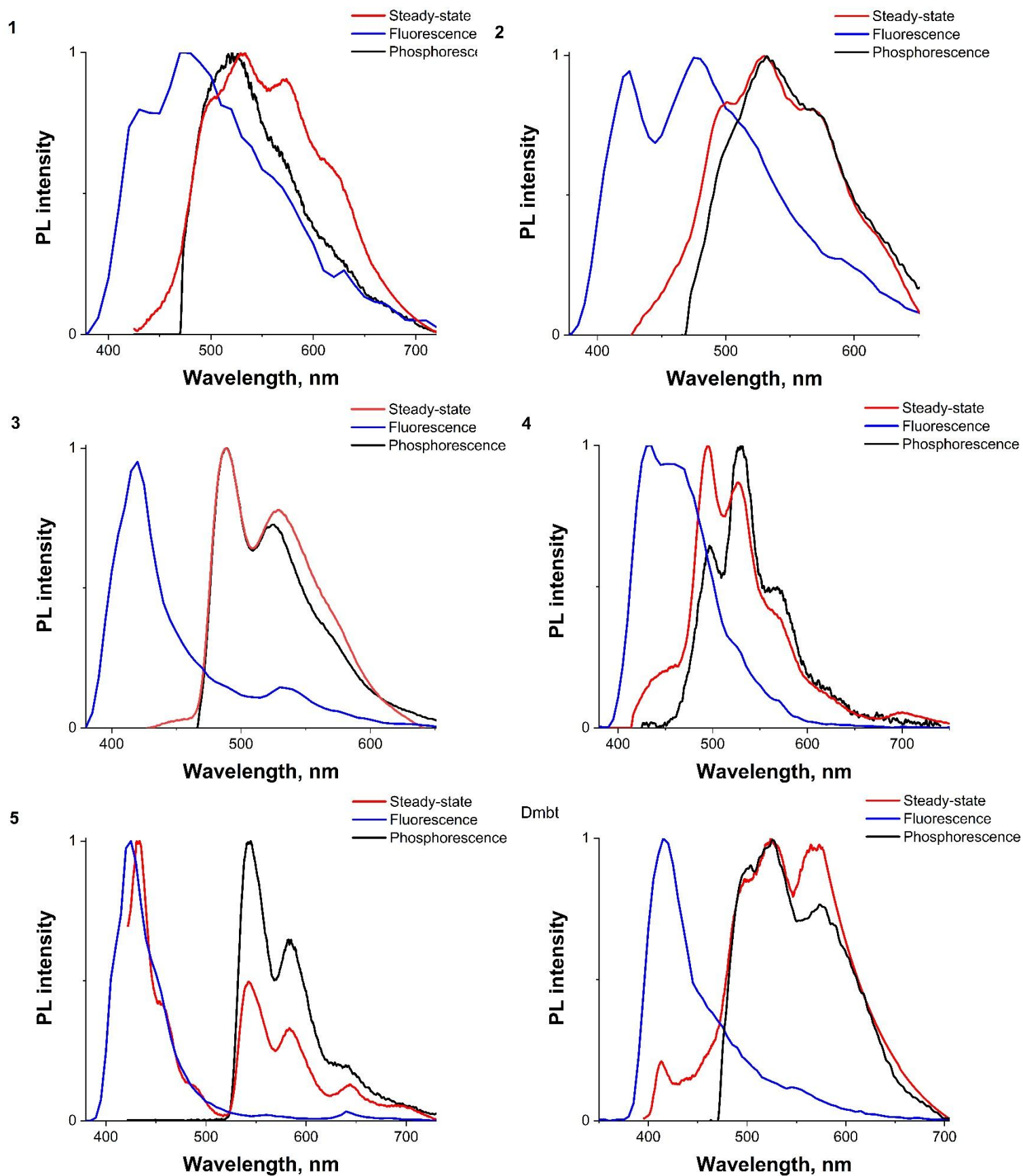


Figure 6S. Steady-state, fluorescence and phosphorescence PL spectra of disodium salts of bithiazoles H₂(dmbt) and **1-5** in DME solutions at 77 K.

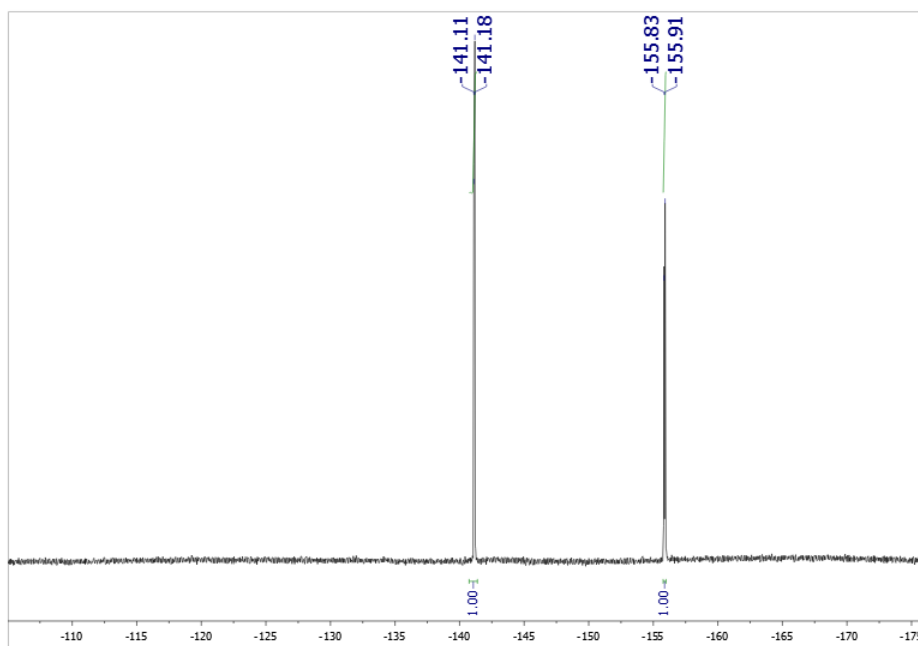


Figure 7S. ^{19}F NMR spectrum of **1** in DME.

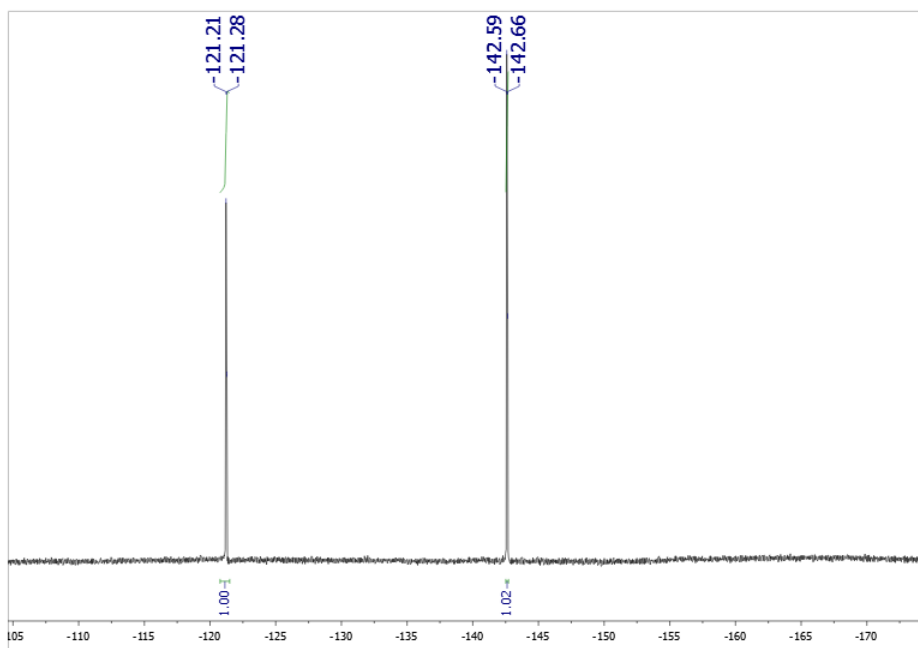


Figure 8S. ^{19}F NMR spectrum of **2** in DME

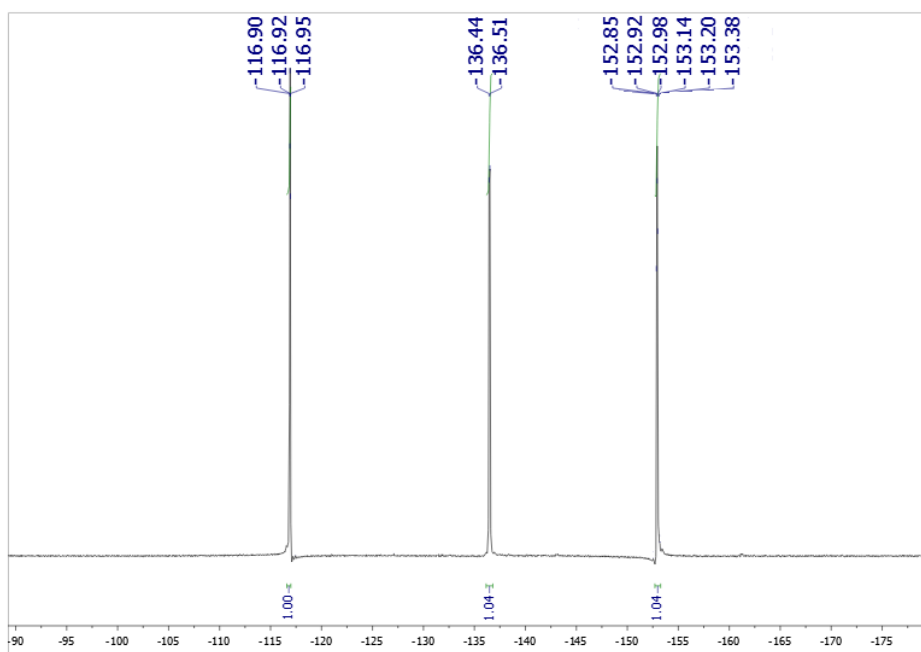


Figure 9S. ^{19}F NMR spectrum of **3** in DME.

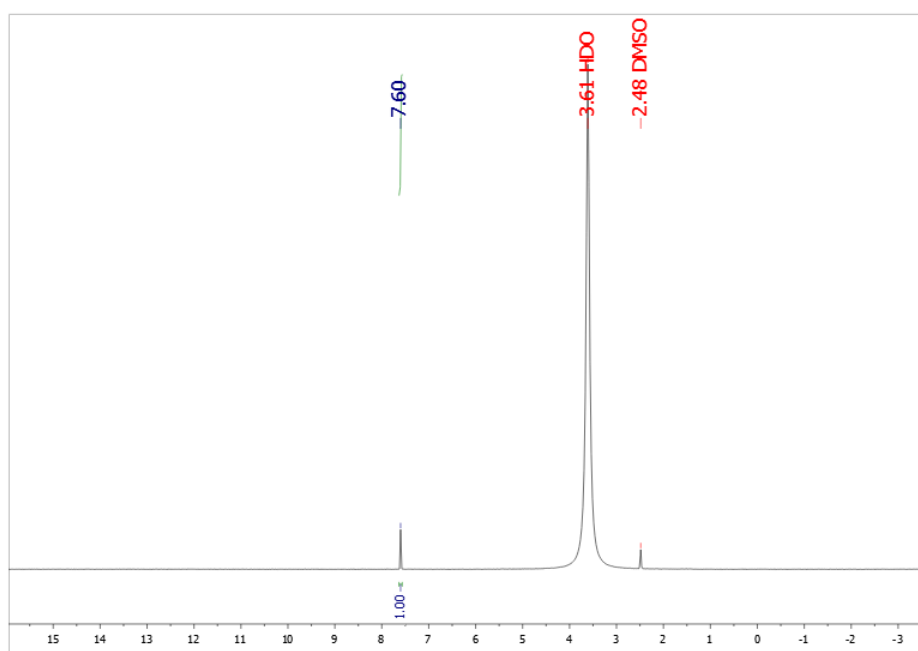


Figure 10S. ^1H NMR spectrum of **4** in $\text{d}_6\text{-DMSO}$.

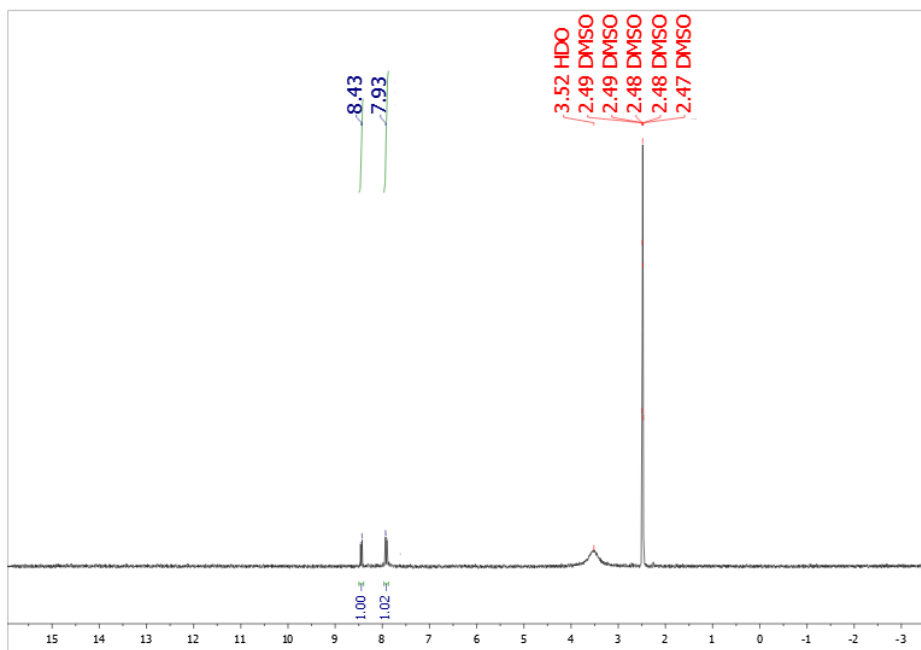


Figure 11S. ^1H NMR spectrum of **5** in $\text{d}_6\text{-DMSO}$.

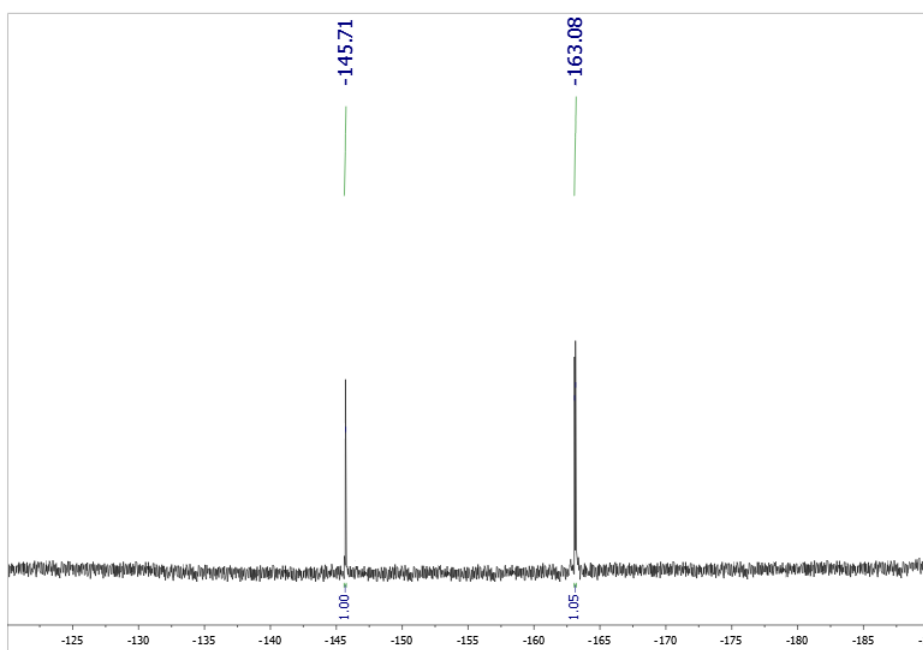


Figure 12S. ^{19}F NMR spectrum of $\text{Na}_2\text{L}^1(\text{DME})_4$ in DME.

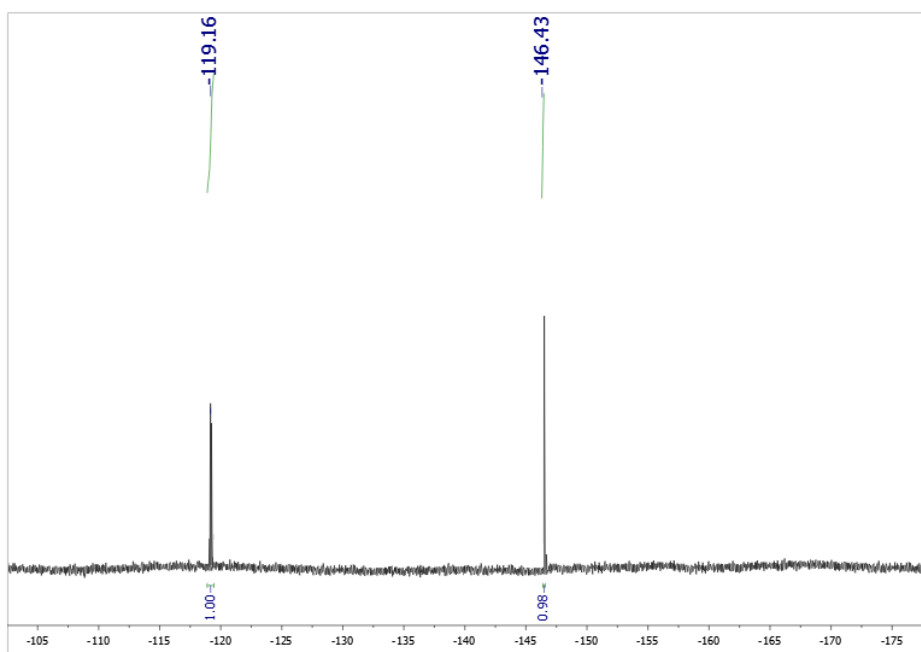


Figure 13S. ^{19}F NMR spectrum of $\text{Na}_2\text{L}^2(\text{DME})_4$ in DME.

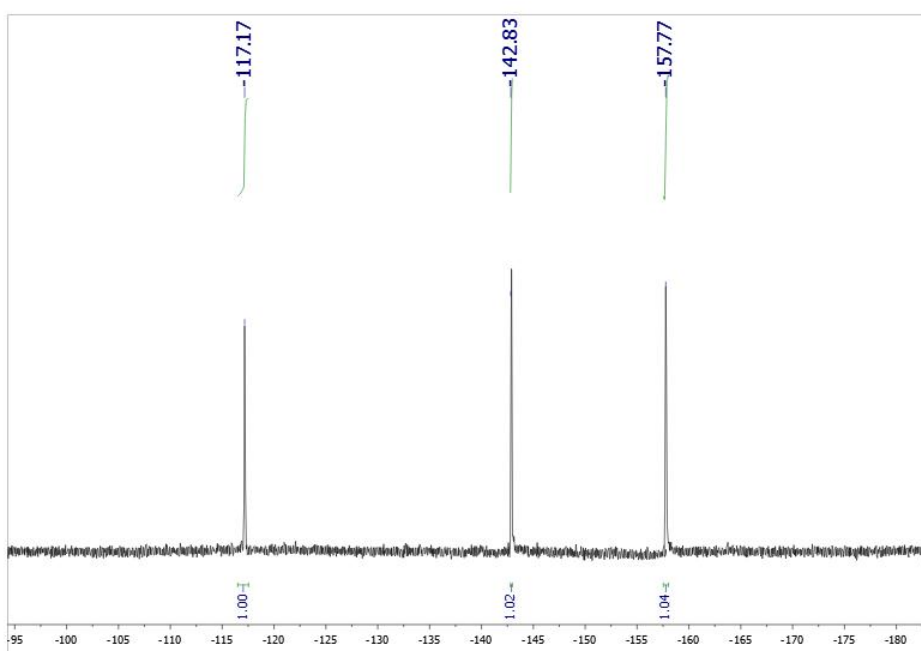


Figure 14S. ^{19}F NMR spectrum of $\text{Na}_2\text{L}^3(\text{DME})_4$ in DME.

046 Rbogzhin2 #448-485 RT: 3.37-3.62 AV: 38 NL: 2.15E6
T: + c Full ms [50.00-400.00]

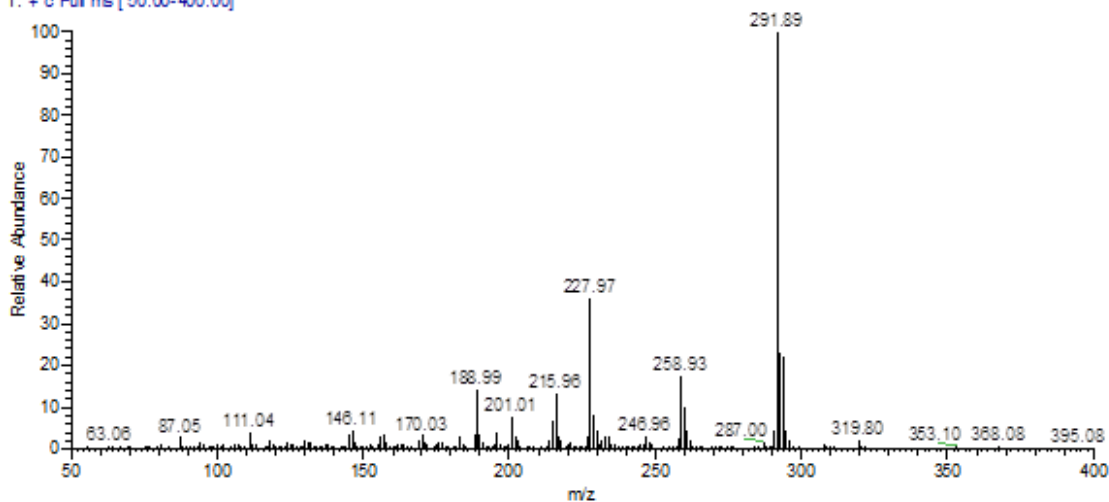


Figure 15S. Mass-spectrum of mixture of 1 and 2.

053 Ilichev1 #327-386 RT: 3.23-3.80 AV: 60 NL: 1.05E6
T: + c Full ms [50.00-700.00]

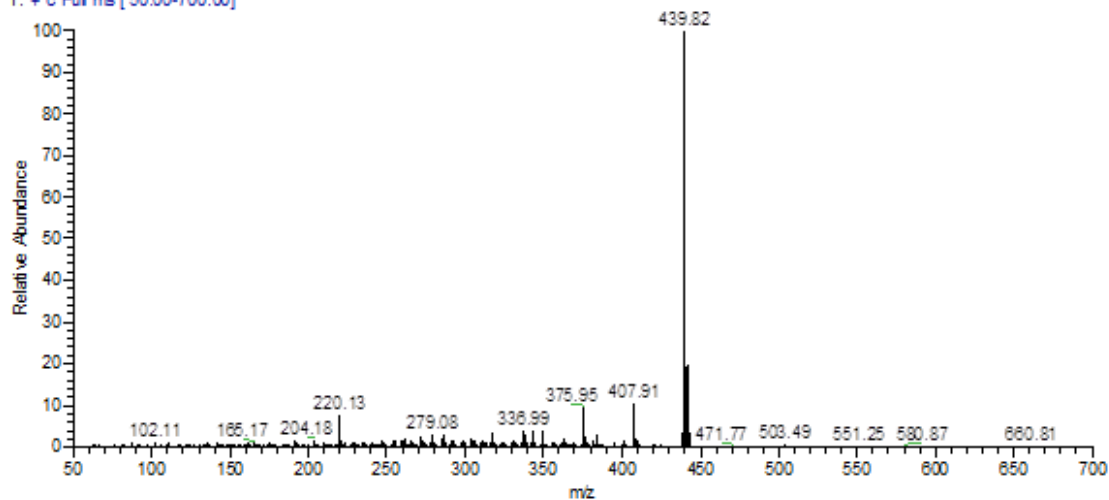


Figure 16S. Mass-spectrum of 3.

036 Rbogzhin1 #585-624 RT: 4.51-4.80 AV: 40 NL: 2.93E5
T: + c Full ms [30.00-400.00]

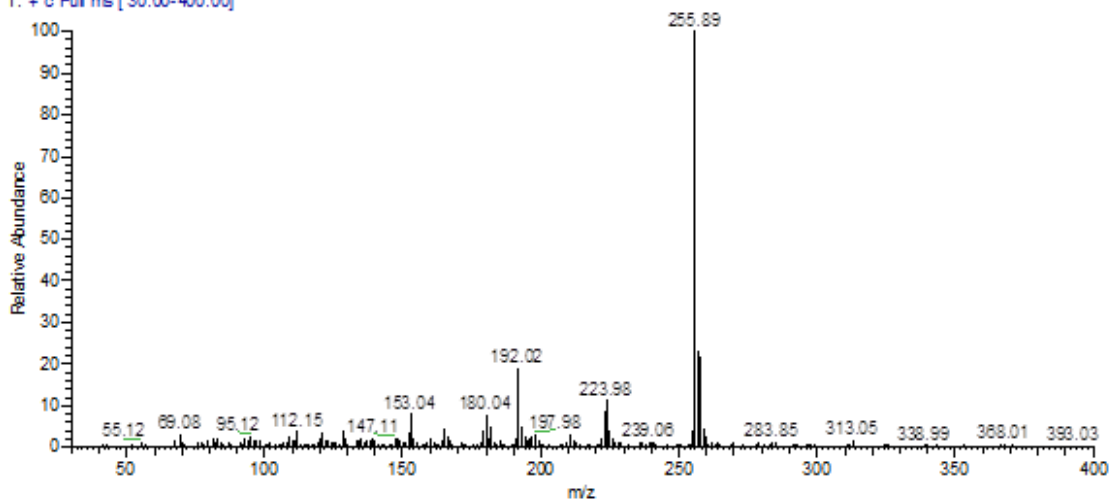


Figure 17S. Mass-spectrum of 4.

015 Rogozhin1 #575-610 RT: 4.86-5.16 AV: 36 NL: 5.18E4
T: + c Full ms [50.00-500.00]

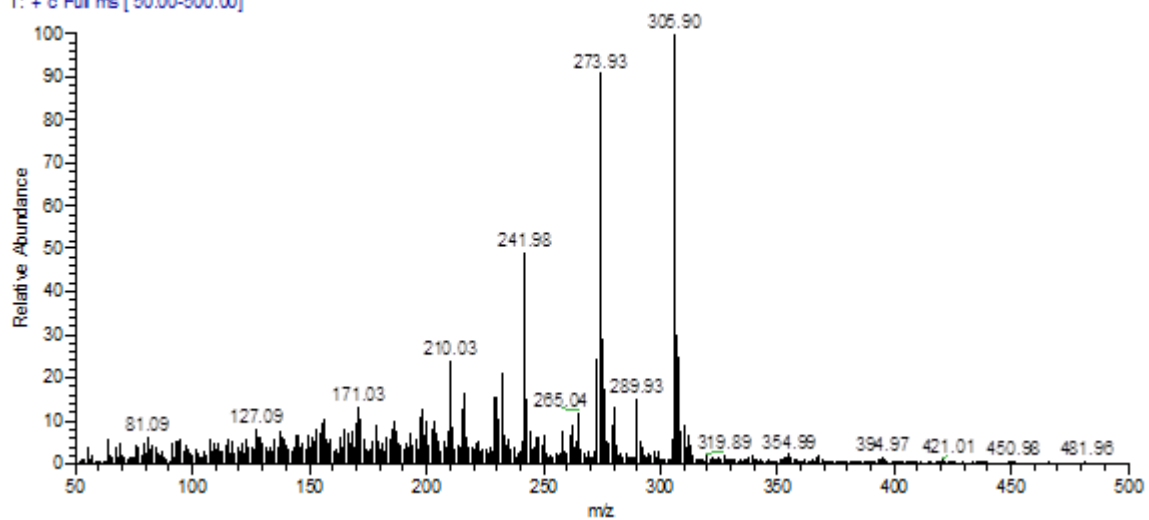


Figure 18S. Mass-spectrum of **5**.

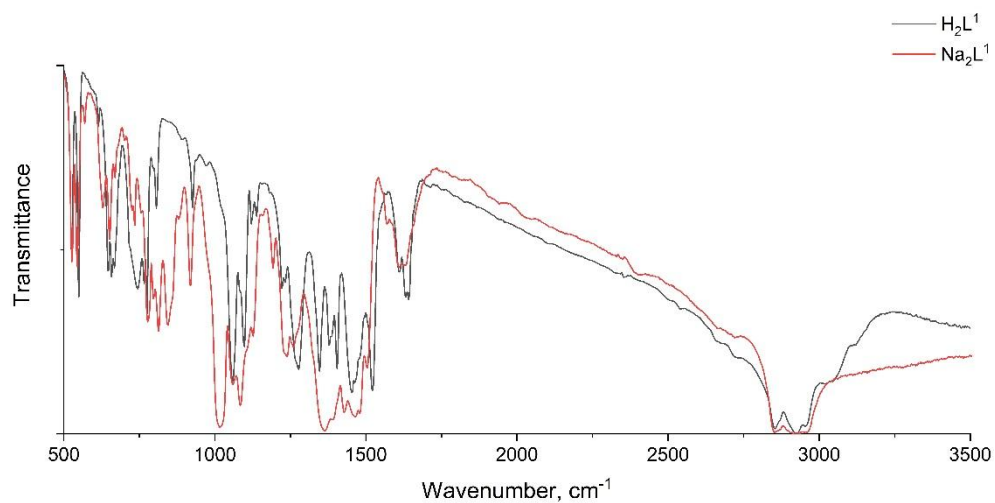


Figure 19S. FTIR spectra of **1** and $\text{Na}_2\text{L}^1(\text{DME})_4$.

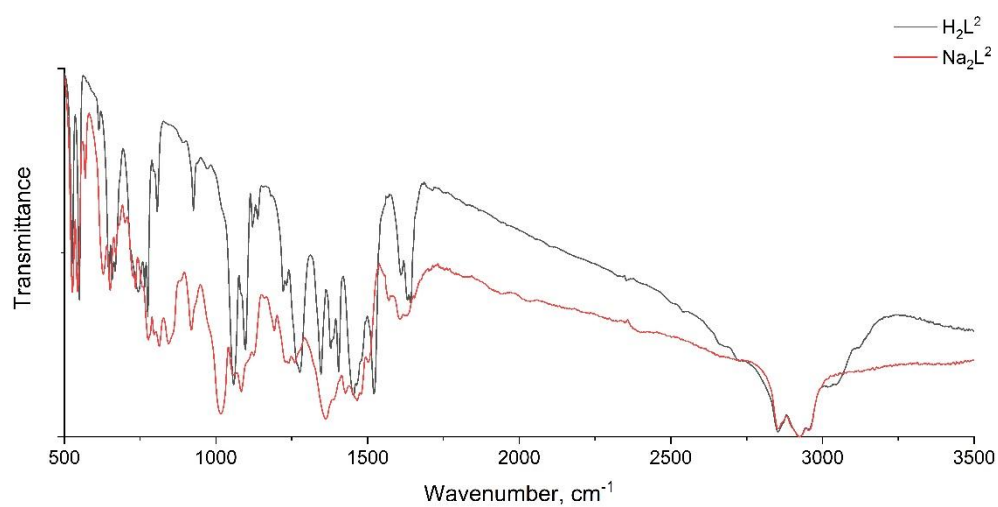


Figure 20S. FTIR spectra of **2** and $\text{Na}_2\text{L}^2(\text{DME})_4$.

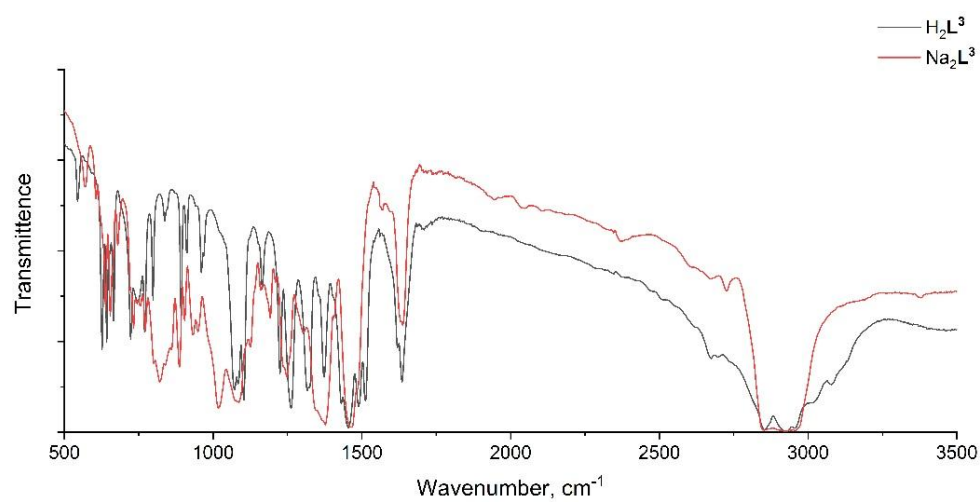


Figure 21S. FTIR spectra of **3** and $\text{Na}_2\text{L}^3(\text{DME})_4$.

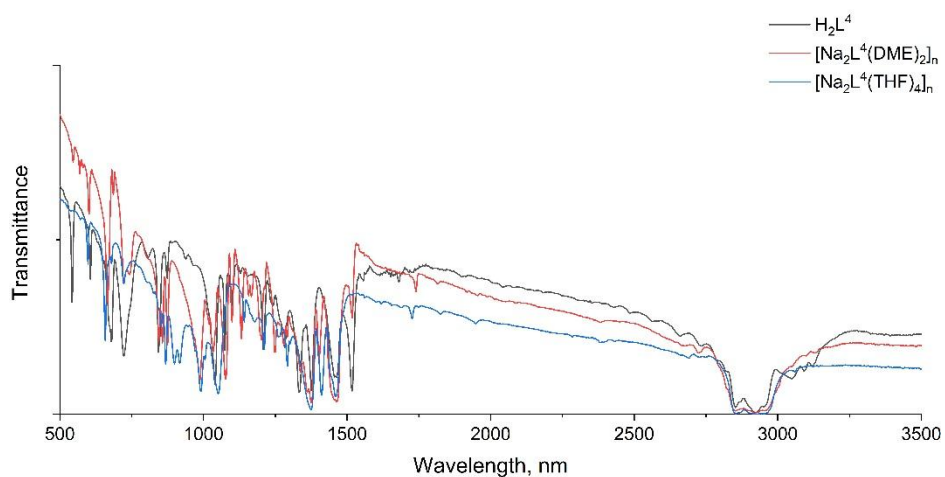


Figure 22S. FTIR spectra of **4**, $[\text{Na}_2\text{L}^4(\text{DME})_2]_n$ and $[\text{Na}_2\text{L}^4(\text{THF})_4]_n$.

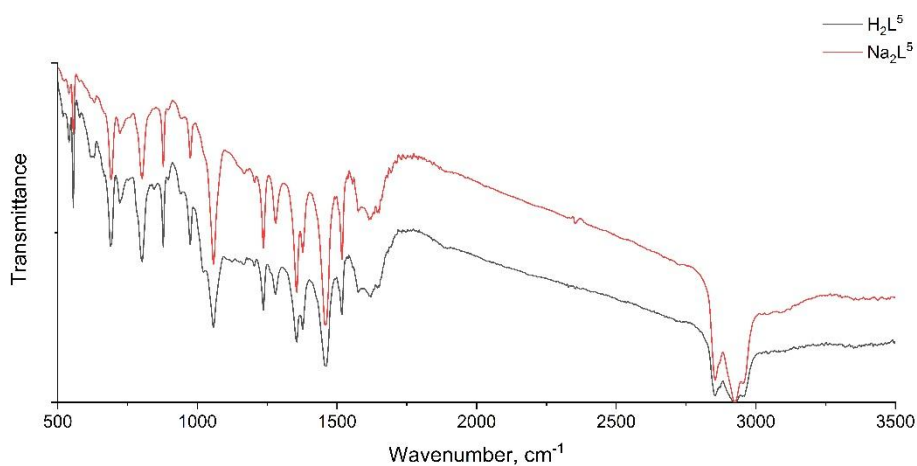


Figure 23S. FTIR spectra of **5** and $\text{Na}_2\text{L}^5(\text{DME})_4$.

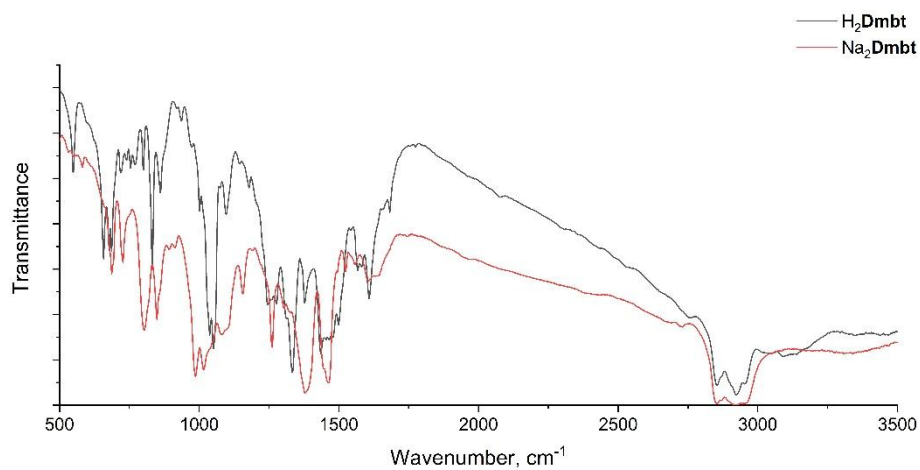


Figure 24S. FTIR spectra of $\text{H}_2(\text{dmbt})$ and $\text{Na}_2\text{dmbt}(\text{DME})_4$.