Supporting Information on

$^{2}_{\infty}[Bi_2Cl_6(pyz)_4]$ – a 2D-pyrazine coordination polymer as soft host lattice for the luminescence of the lanthanide ions Sm^{3+}, Eu^{3+}, Tb^{3+}, and Dy^{3+}

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X-ray single crystal diffraction

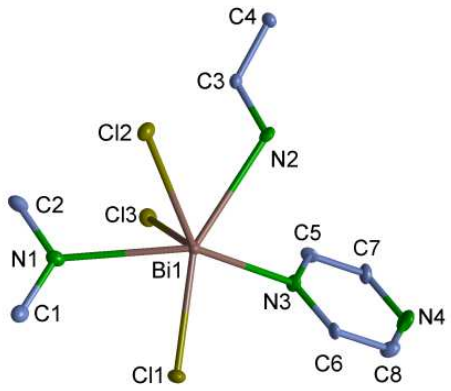

Figure S1. Asymmetric unit of the crystal structure of $^{2}_{\infty}[Bi_2Cl_6(pyz)_4]$ (**1**), ellipsoids with 30% probability.

Table S1: Crystallographic data on $^{2}_{\infty}[Bi_2Cl_6(pyz)_4]$ (**1**), deviations given in brackets.

Formula	C8 H8 Bi Cl3 N4
Fw (g mol^{-1})	475.51
Crystal color/shape	Colorless plate
Crystal size (mm^3)	0.1x0.05x0.2
Radiation, λ (Å)	Mo K_α, 0.71073
Crystal system	triclinic
Space group	P-1
a (Å)	7.7661(8)
b (Å)	9.6245(10)
c (Å)	9.9385(10)
α (deg)	107.2290(10)
β (deg)	110.7940(10)
γ (deg)	98.0680(10)
V/ Å^3	637.74(11)
Z	2
ρ_{calcd} (g cm^{-3})	2.476
μ (Mo Kα) (mm^{-1})	14.429
Absorption correction type	multi-scan
Min/max transmission	0.5309/ 0.7464
Data range (deg)	$2.60 \leq 2\theta \leq 64.46°$
Collected reflections	10480

R(int)	0.1291
Independent reflections	4111
Independent reflections (I > 2σ(I))	3857
Parameters	145
R_1 (I > 2σ(I))	0.0419
wR_2 (all data)	0.1153
S (all data)	1.141
Residual electron density ($e^{-}\cdot Å^{-3}$)	4.565/-3.328

Table S2: Selected interatomic distances (in A) and angles (in °) in **1**.

Symmetry operation: I-x, -y, -z

Bi1-Cl1	2.563(2)
Bi1-Cl2	3.0537(17)
Bi1-Cl2^{I}	2.8263(17)
Bi1-Cl3	2.5724(17)
Bi1-N1	2.750(7),
Bi1-N2	2.719(8)
Bi1-N3	2.491(6)
Cl1-Bi1-Cl2^{I}	89.19(7)
Cl1-Bi1-Cl2	133.04(6)
Cl1-Bi1-Cl3	101.58(7)
Cl1-Bi1-N1	78.11(15)
Cl1-Bi1-N2	153.34(13)
Cl2-Bi1-Cl2^{I}	80.08(5)
Cl3-Bi1-Cl2^{I}	157.93(7)
Cl3-Bi1-Cl2	105.17(5)
Cl3-Bi1-N1	77.75(14)
Cl3-Bi1-N2	80.97(14)
N1-Bi1-Cl2^{I}	123.69(13)
N1-Bi1-Cl2	70.91(14)
N2-Bi1-Cl2	69.68(12)
N2-Bi1-Cl2^{I}	80.92(14)
N2-Bi1-N1	127.81(19)
N3-Bi1-Cl1	80.18(17)
N3-Bi1-Cl2	140.18(17)
N3-Bi1-Cl2^{I}	79.25(15)
N3-Bi1-Cl3	83.64(15)
N3-Bi1-N1	147.8(2)
N3-Bi1-N2	73.7(2)

X-ray powder diffraction

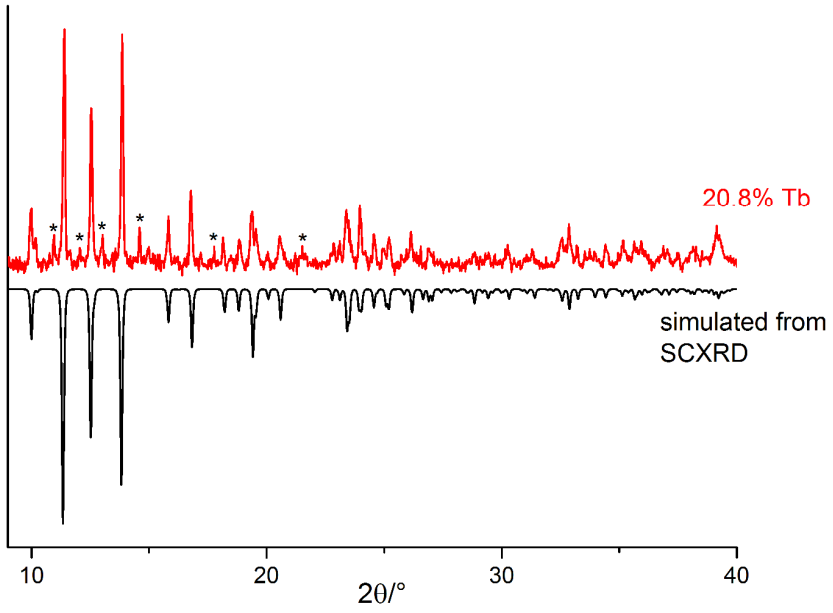

Figure S2. Powder diffraction pattern of bulk **4** with a terbium content of 20.8% and the pattern simulated from single crystal data with reflections from an unknown secondary phase marked with *.

Photoluminescence spectroscopy

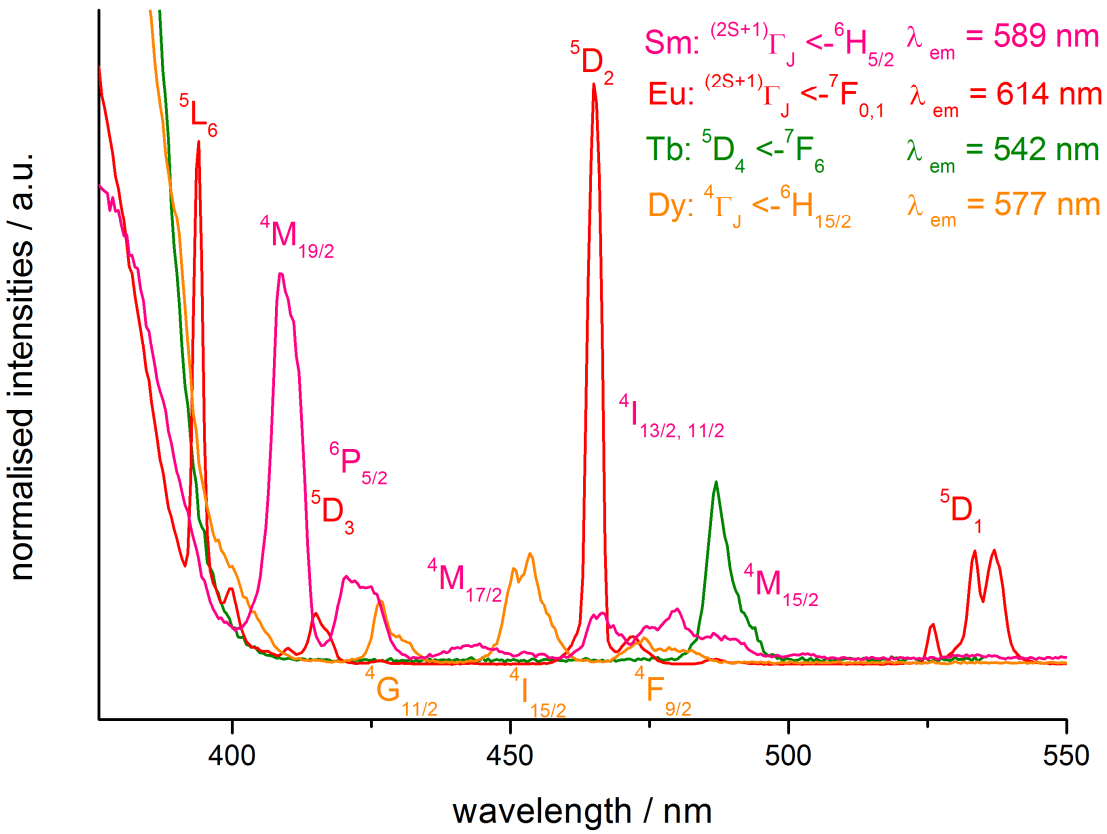

Figure S3. Detailed view of the excitation spectra of $^2{}_\infty[Bi_{(2-x)}Ln_xCl_6(pyz)_4]$ (Sm: **2**, Eu: **3**, Tb: **4**, Dy: **5**) (lanthanide contents: Sm: 5.6 %; Eu: 3.2 %; Tb: 4.6 %; Dy: 4.6 %) at room temperature with an assignment of the respective *ff*-transitions. Note that the assignment of transitions remains tentative for Sm^{3+} in **2**, as a number of closely spaced and possibly interacting transitions can be observed in this region of the spectrum.

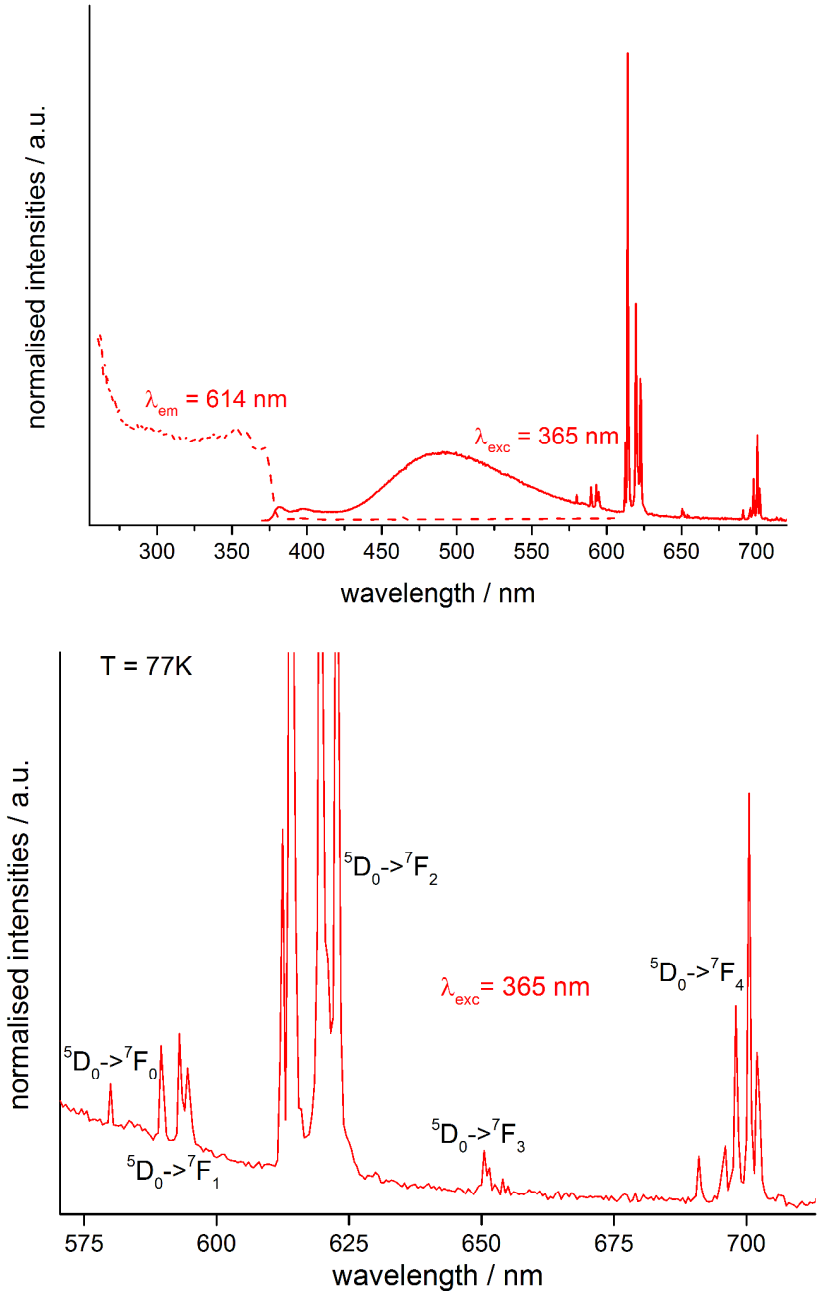

Figure S4. Excitation and emission spectrum of $^{2}_{\infty}[Bi_{(2-x)}Eu_xCl_6(pyz)_4]$ (**3**) (europium content: 3.2 %) at 77 K (top) and detailed view of the emission spectrum (bottom).

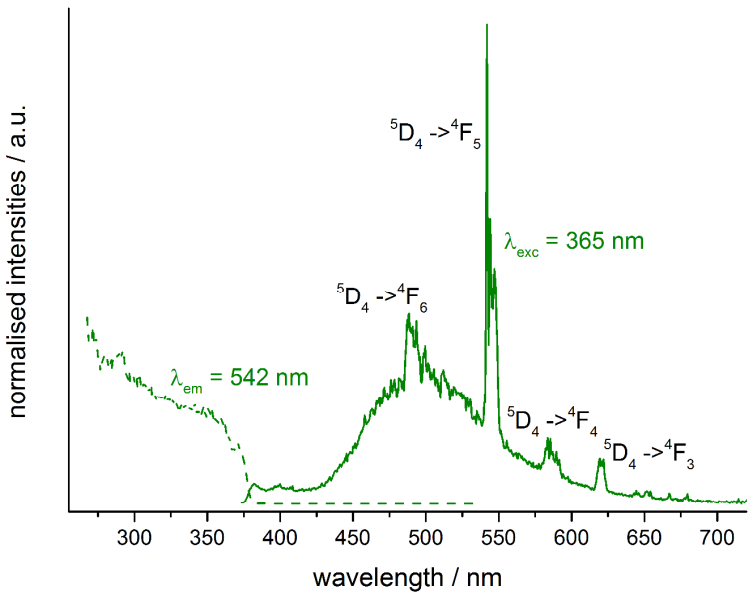

Figure S5. Excitation and emission spectrum of $^2{}_\infty[Bi_{(2-x)}Tb_xCl_6(pyz)_4]$ (**4**) (terbium content: 4.6 %) at 77 K.

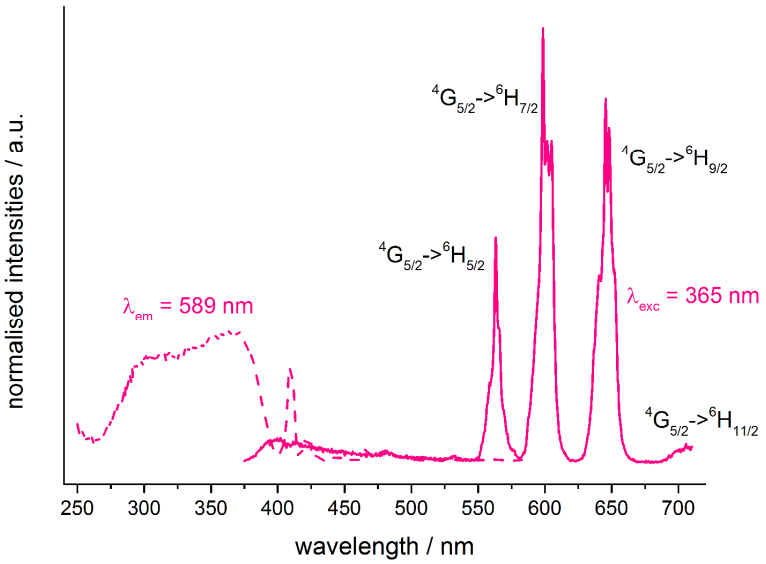

Figure S6. Excitation and emission spectrum of $^2{}_\infty[Bi_{(2-x)}Sm_xCl_6(pyz)_4]$ (**2**) (samarium content: 5.6 %) at room temperature.

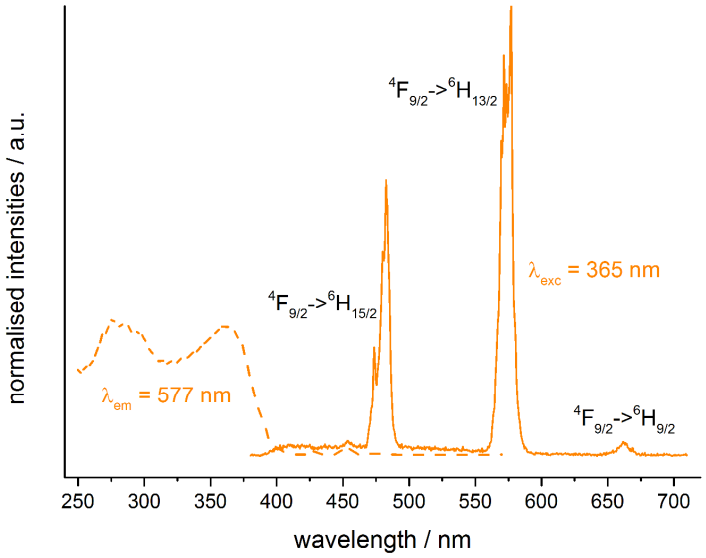

Figure S7. Excitation and emission spectrum of $^2{}_\infty[Bi_{(2-x)}Dy_xCl_6(pyz)_4]$ (**5**) (europium content: 4.6 %) at room temperature.

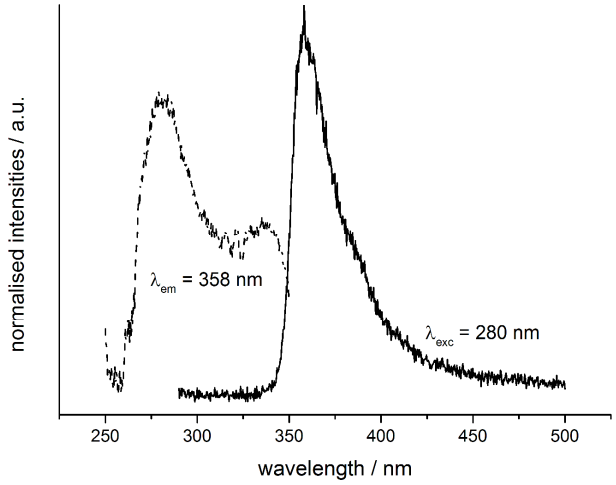

Figure S8. Excitation and Emission spectrum of pyrazine at room temperature.

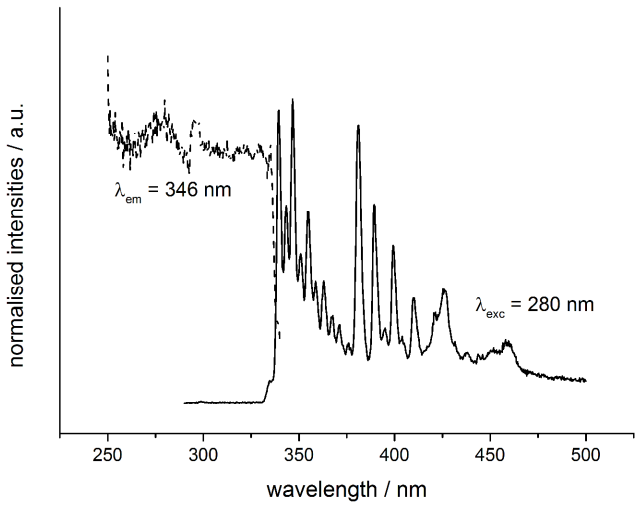

Figure S9. Excitation and Emission spectrum of pyrazine at 77 K, displaying the typical fluorescence (336-377 nm) and phosphorescence (377-472 nm) bands. [S1]

Thermal analysis

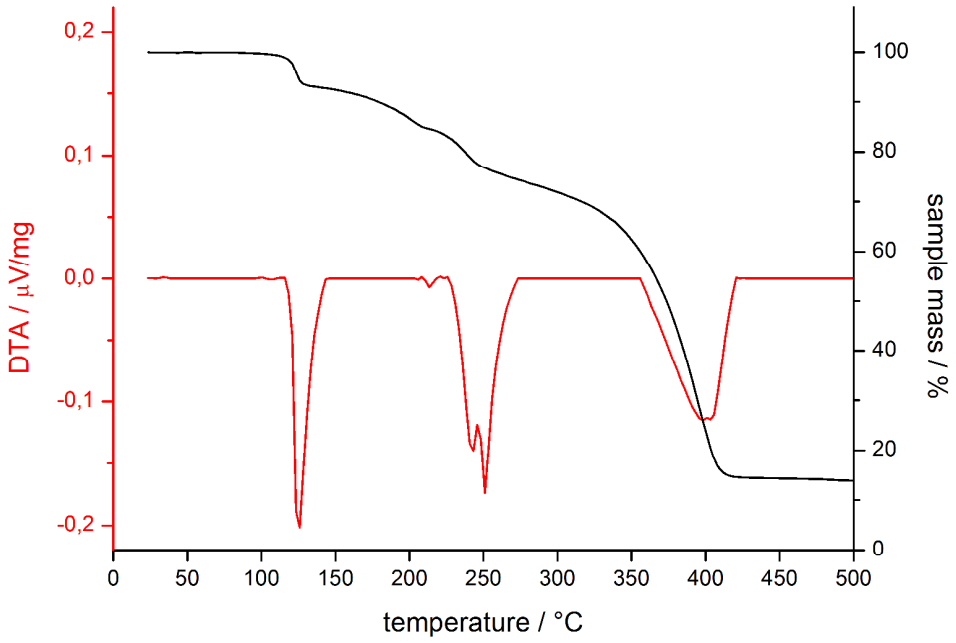

Figure S10. Simultaneous DTA/TG of **1**.

^{13}C-Solid State NMR

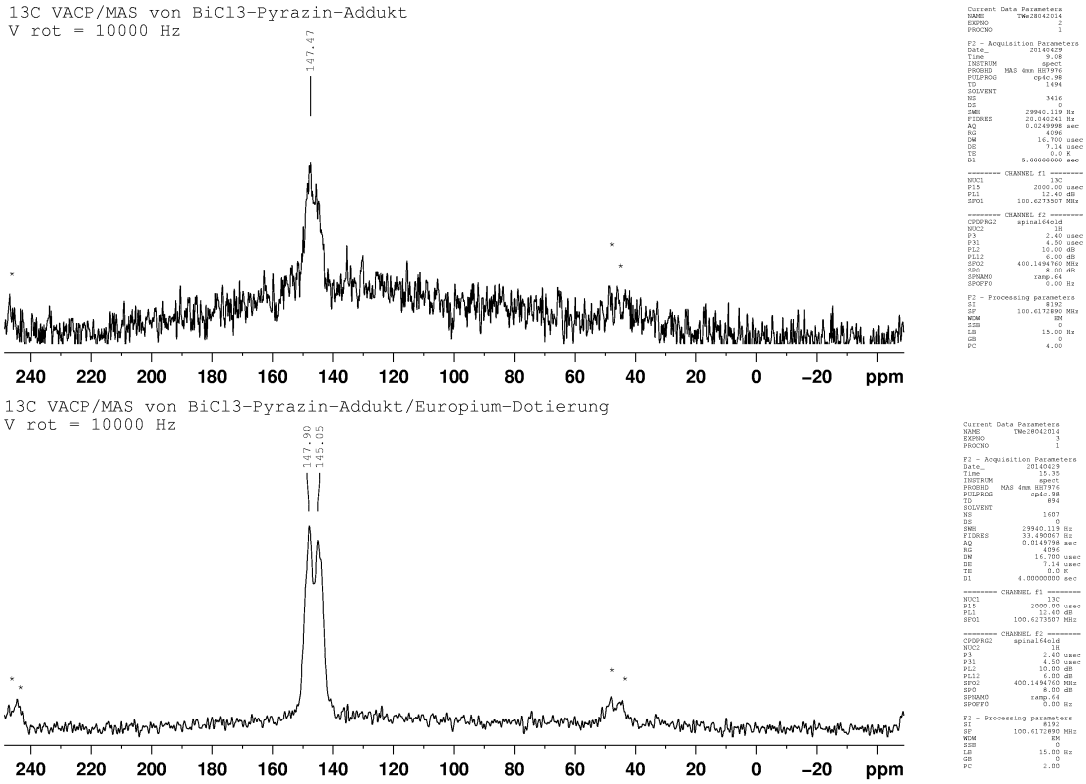

Figure S11. ^{13}C-Solid State NMR of **1** (top) and 3 (4.0-at% europium, bottom) both displaying a doublet at the same chemical shift. Rotational side bands are marked by an *.

References

(S1) McDonald, R. J.; Logan, L. M.; Ross, I. G.; Selinger, B. K. *J. Mol. Spec.* **1971**, *40*, 137-143.