Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Crystallographic characterization of ethylammonium salts of tetracyanopyridine (TCPy) and fluorescent determination of the degree of substitution of the amino nitrogen atom using thereof

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1. Luminescent properties

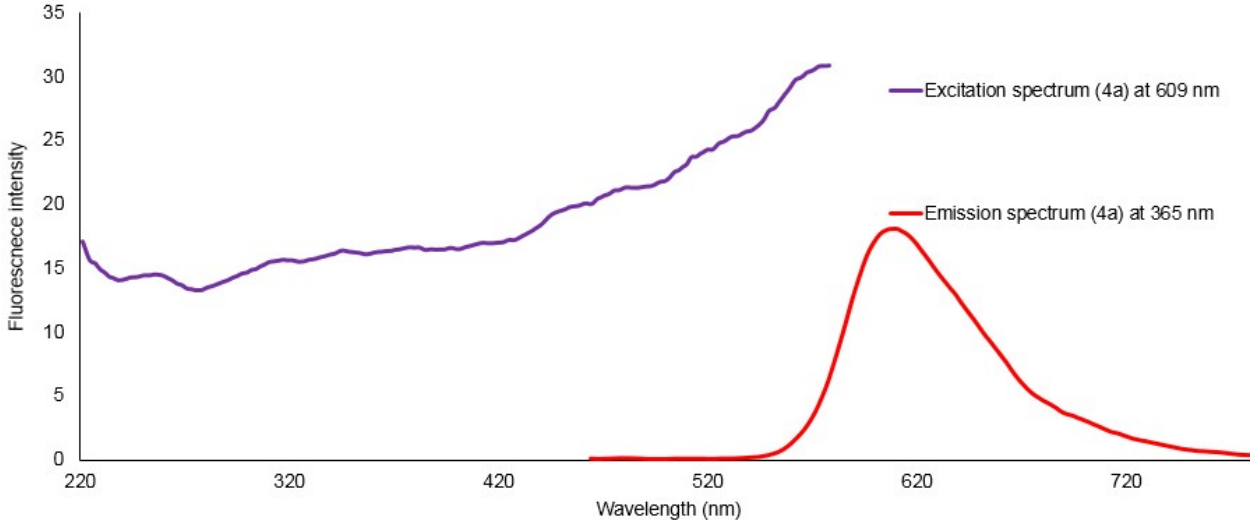

Figure S1 Excitation and emission spectra **4a** in the solid state.

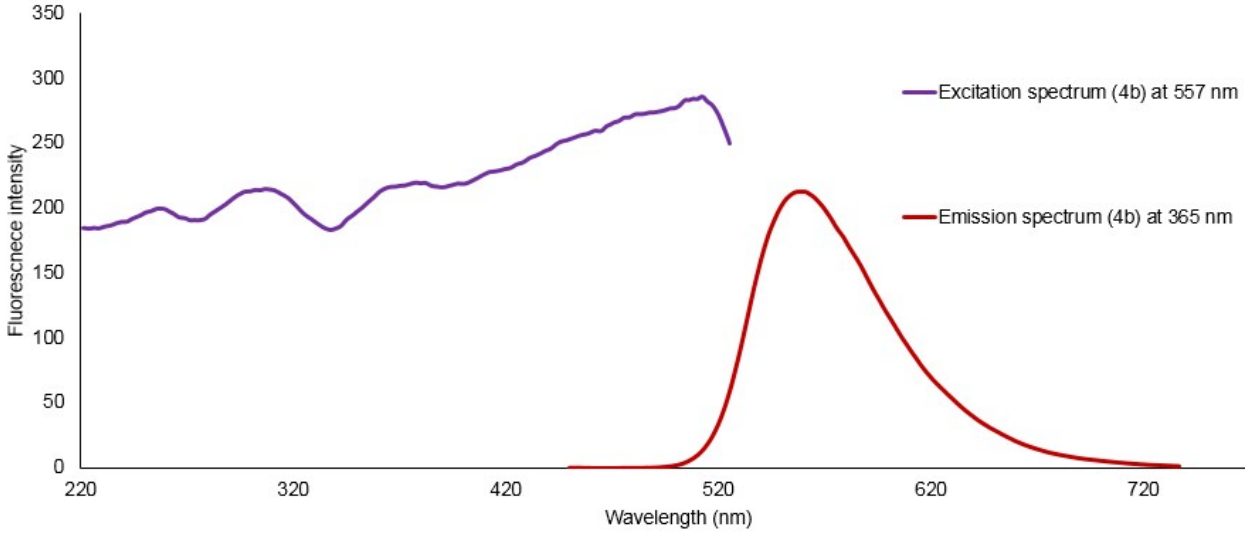

Figure S2 Excitation and emission spectra **4b** in the solid state.

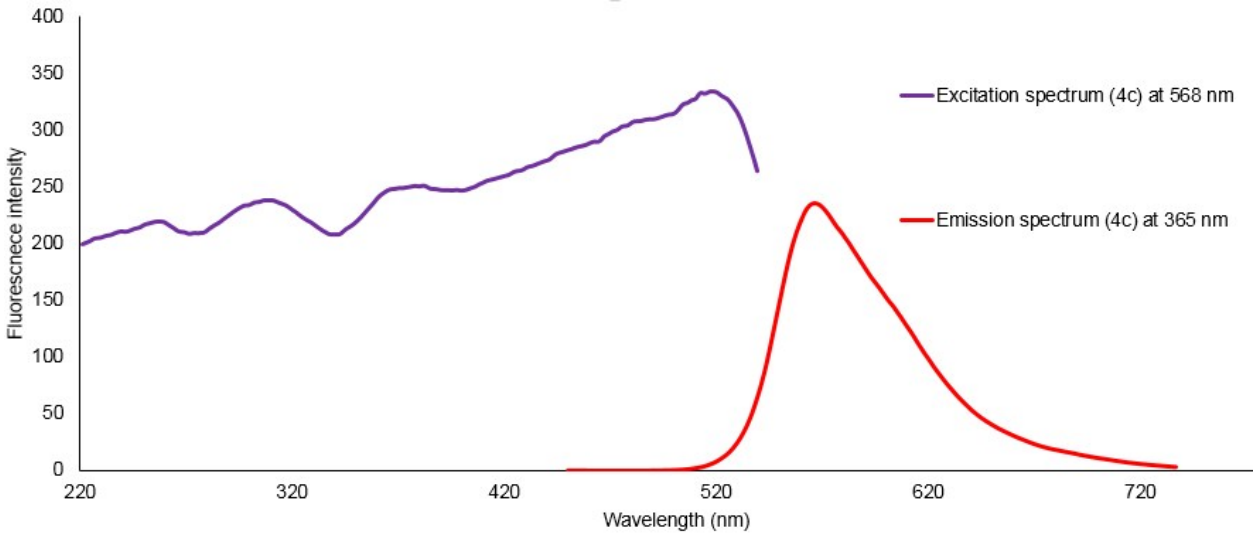

Figure S3 Excitation and emission spectra **4c** in the solid state.

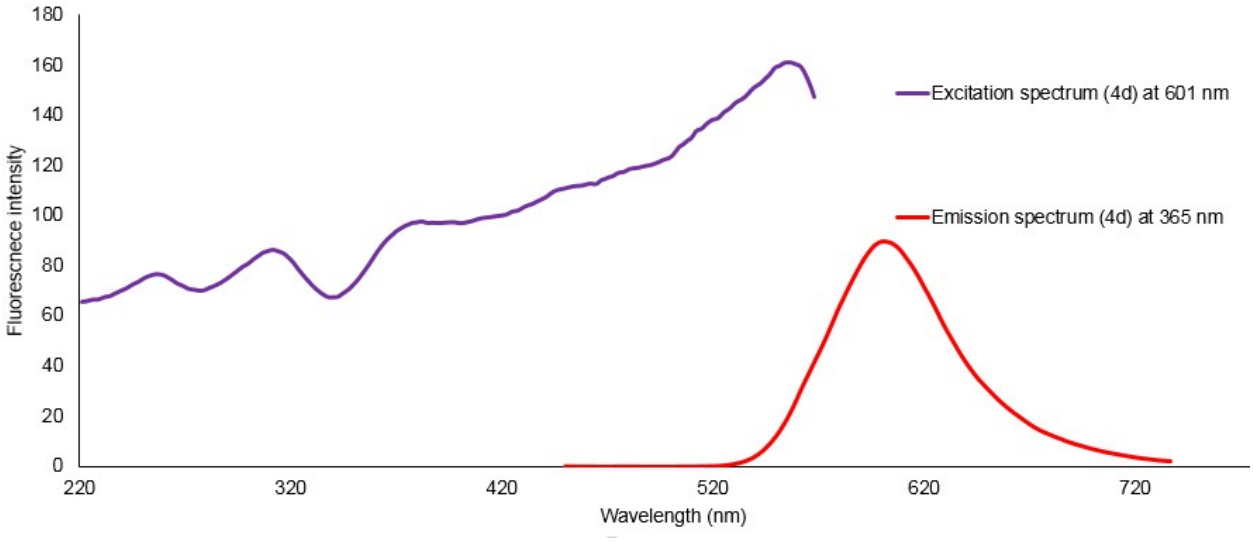

Figure S4 Excitation and emission spectra **4d** in the solid state.

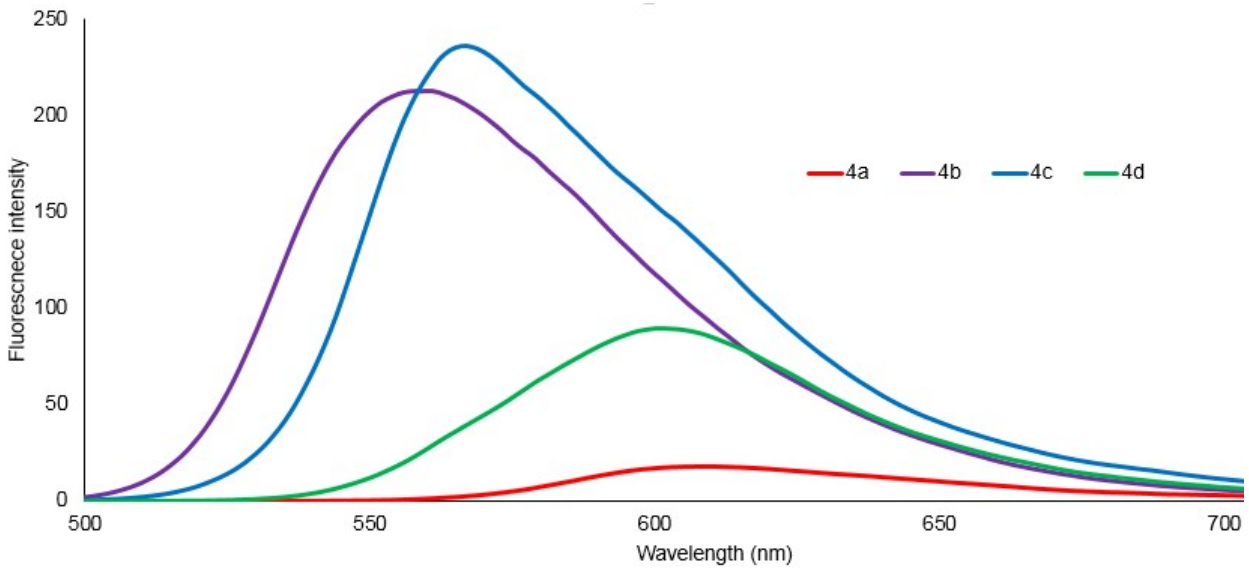

Figure S5 Emission spectra of solid-state emission **4a-d** (excitation wavelength 365 nm).

2. XRD data

Crystals of each salt that were suitable for X-ray diffraction study were obtained by slow evaporation of a solution of the appropriate salt in acetonitrile at room temperature

Table S1 Hydrogen bonds for **4a**-**d** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
4a				
N6-H6A...N2	0.89	2.28	2.895(12)	126.5
N6-H6A...N4[1]	0.89	2.39	3.070(13)	133.6
N6-H6B...N3A	0.89	2.02	2.851(15)	153.9
N6-H6C...N1A[2]	0.89	2.34	3.222(12)	170.1
C20-H20C...N4[1]	0.96	2.57	3.277(17)	130.7
N6A-H6A1...N1[3]	0.89	2.32	3.147(11)	154.2
N6A-H6A2...N3	0.89	2.13	2.886(15)	142.9
N6A-H6A3...N2A[4]	0.89	2.12	2.934(13)	150.9
N6A-H6A3...N4A[3]	0.89	2.64	3.067(14)	110.5
Symmetry transformations used to generate equivalent atoms: (i) -x+1,y+1/2,-z+3/2; (ii) -x+2,y+1/2,-z+3/2; (iii) -x+1,y-1/2,-z+3/2; (iv) x-1,y,z				
4b				
C21-H21C...N5[1]	0.96	2.61	3.558(16)	168.8
N6-H61...N2[2]	0.928(14)	2.04(3)	2.925(10)	159(8)
N6-H62...N3	0.924(14)	2.30(6)	3.013(11)	133(7)
N6-H62...N4[1]	0.924(14)	2.52(6)	3.251(10)	136(7)
Symmetry transformations used to generate equivalent atoms: (i) x+1,y,z; (ii) -x+2,y-1/2,-z+1/2				
4c				
N6-H6...N2B[1]	0.98	1.90	2.855(7)	163.9
C19-H19A...N1C[2]	0.97	2.58	3.516(8)	161.5
C21-H21B...N4B[3]	0.97	2.61	3.330(9)	131.0
C23-H23B...N4C[3]	0.97	2.67	3.611(10)	164.1
N6A-H6A...N2C[2]	1.01	1.88	2.887(8)	176.5
C19A-H19C...N3B[4]	0.97	2.68	3.436(11)	135.2
C19A-H19D...N4C[3]	0.97	2.63	3.583(12)	168.2
N6B-H6B...N2A[5]	0.94	1.92	2.844(8)	164.0
C21B-H21F...N1[5]	0.97	2.59	3.534(8)	163.1
C23B-H23E...N4[6]	0.97	2.62	3.341(9)	131.8
N6C-H6C...N2[7]	0.98	1.86	2.843(8)	178.1
C19C-H19H...N4[6]	0.97	2.60	3.525(12)	159.8
C23C-H23H...N4A[8]	0.97	2.55	3.513(15)	170.4
Symmetry transformations used to generate equivalent atoms: (i) -x,y-1/2,-z+1; (ii) -x+1,y-1/2,-z+1; (iii) x,y,z-1; (iv) x+1,y,z-1; (v) x,y+1,z; (vi) -x+1,y+1/2,-z+1; (vii) x+1,y+1,z; (viii) -x+2,y+1/2,-z+1				
4d				
C20-H20A...N5[1]	0.97	2.67	3.495(6)	143.1
C20-H20B...N2	0.97	2.58	3.114(7)	115.1
C23-H23A...N2[2]	0.96	2.57	3.431(6)	149.9
C26-H26B...N3[3]	0.97	2.59	3.464(7)	149.2
C201-H20C...N3[3]	0.97	2.55	3.351(9)	140.2
C231-H23F...N2[2]	0.96	2.53	3.431(6)	155.5
C241-H24C...N5[1]	0.97	2.62	3.172(8)	116.0
Symmetry transformations used to generate equivalent atoms: (i) -x+1,-y,-z+2; (ii) x+1,y,z; (iii) -x+1,y+1/2,-z+3/2				

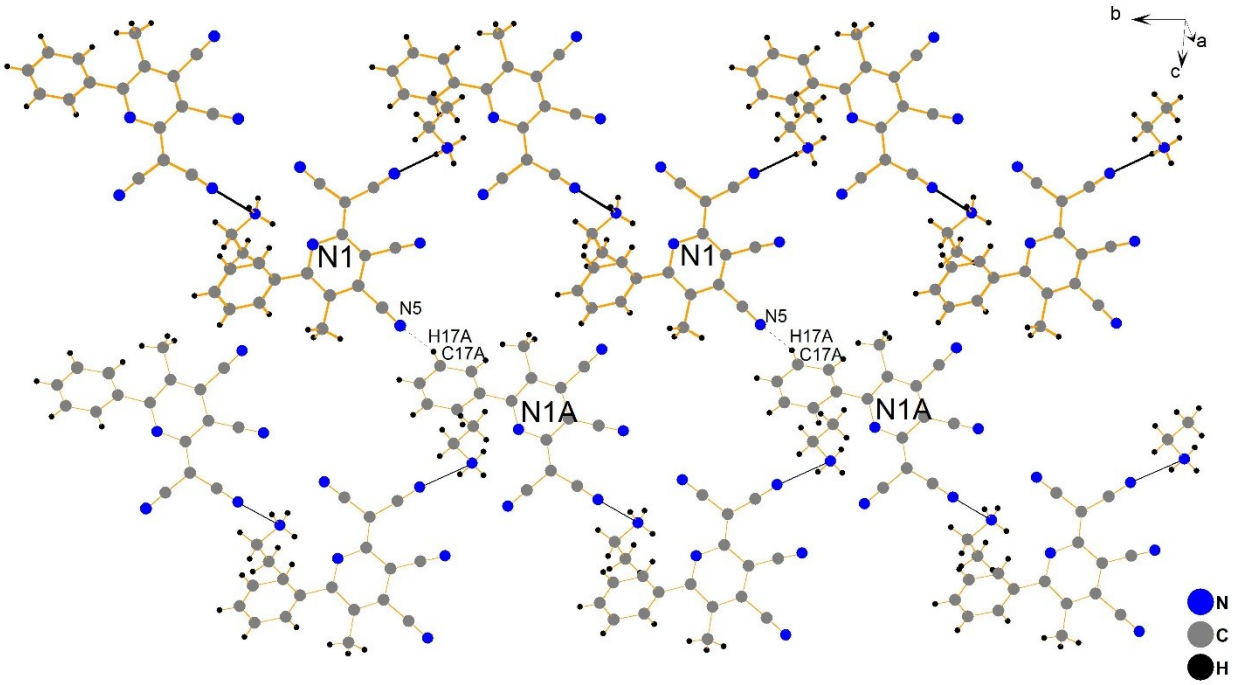

Figure S6 The infinite ribbons in **4a** connected by C–H···N hydrogen bonds. The bottom ribbon is depicted with thinner bonds. The hydrogen bonds are depicted as dashed lines.

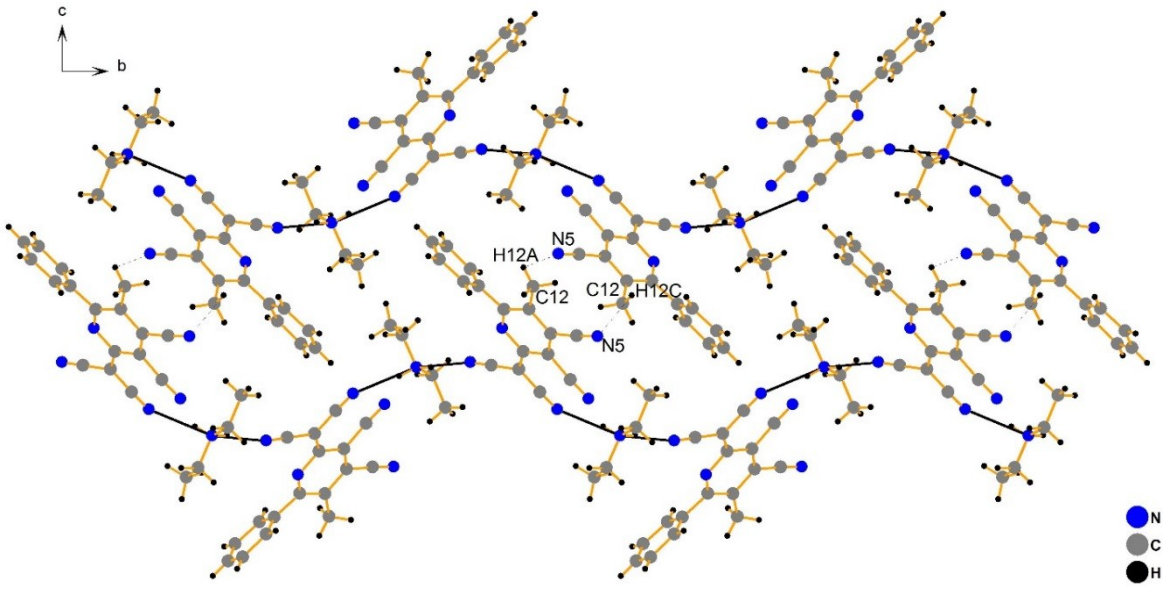

Figure S7 The 2D layer in **4b**. The hydrogen bonds are depicted as dashed lines.

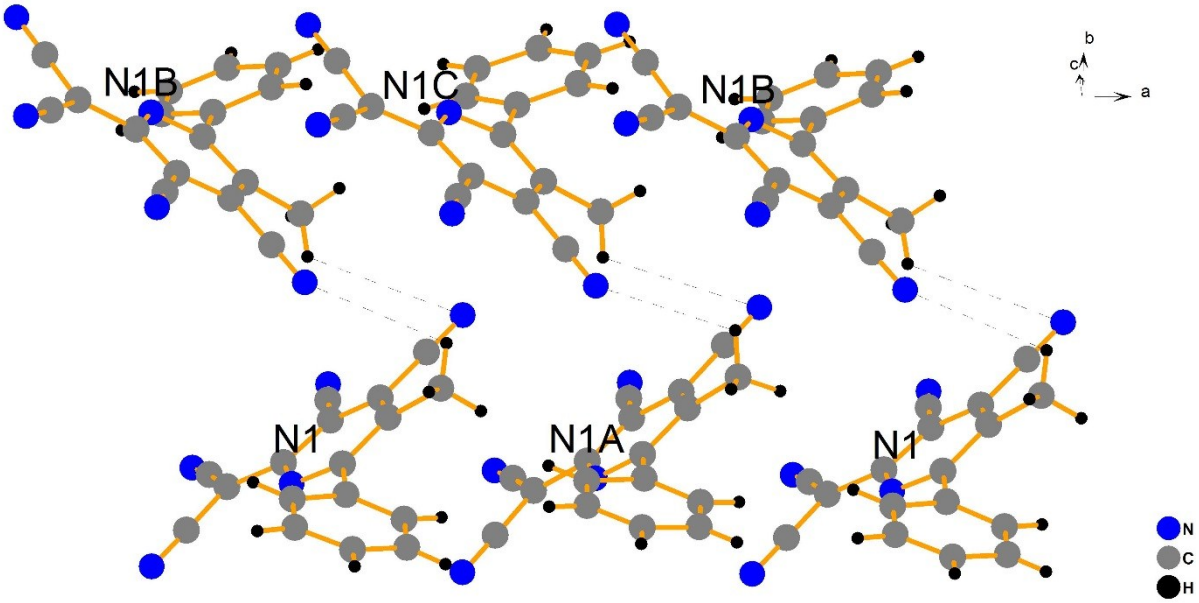

Figure S8 Formation of dimer of $TCPy^-$ in **4c**.

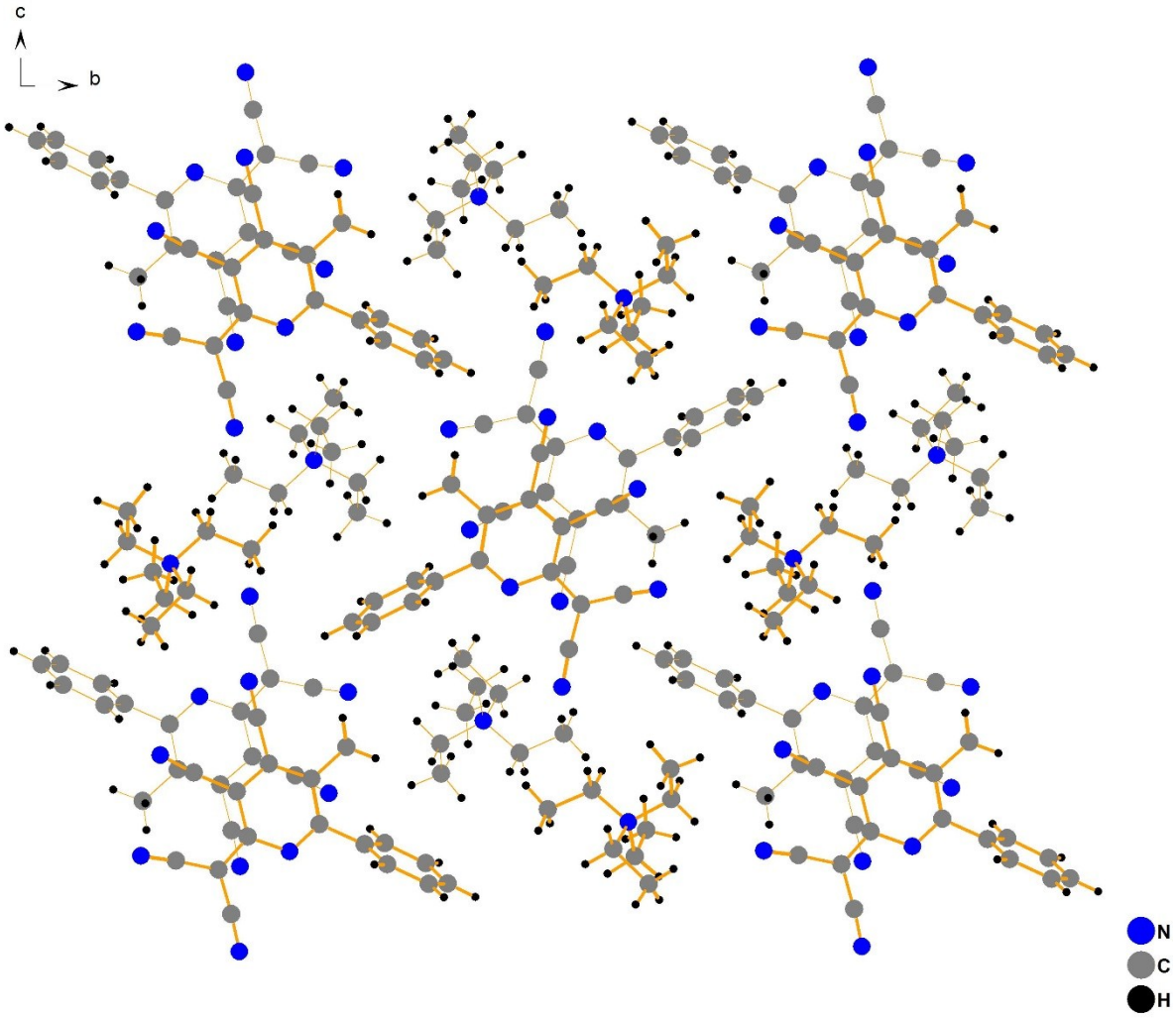

Figure S9 The 2D layer in **4d** The bottom layer is depicted with thinner bonds.

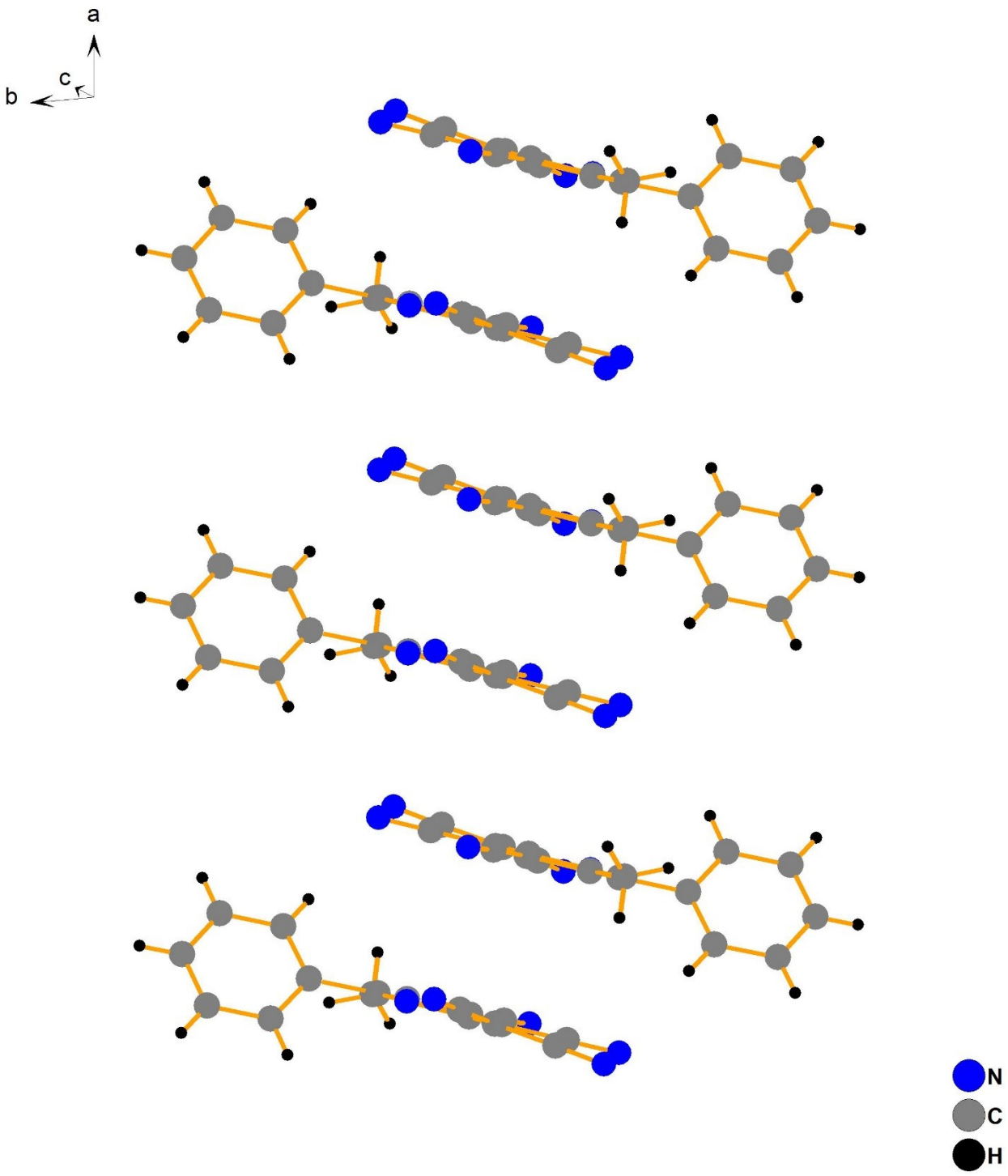

Figure S10 The anion column in **4d**.

3. NMR spectra

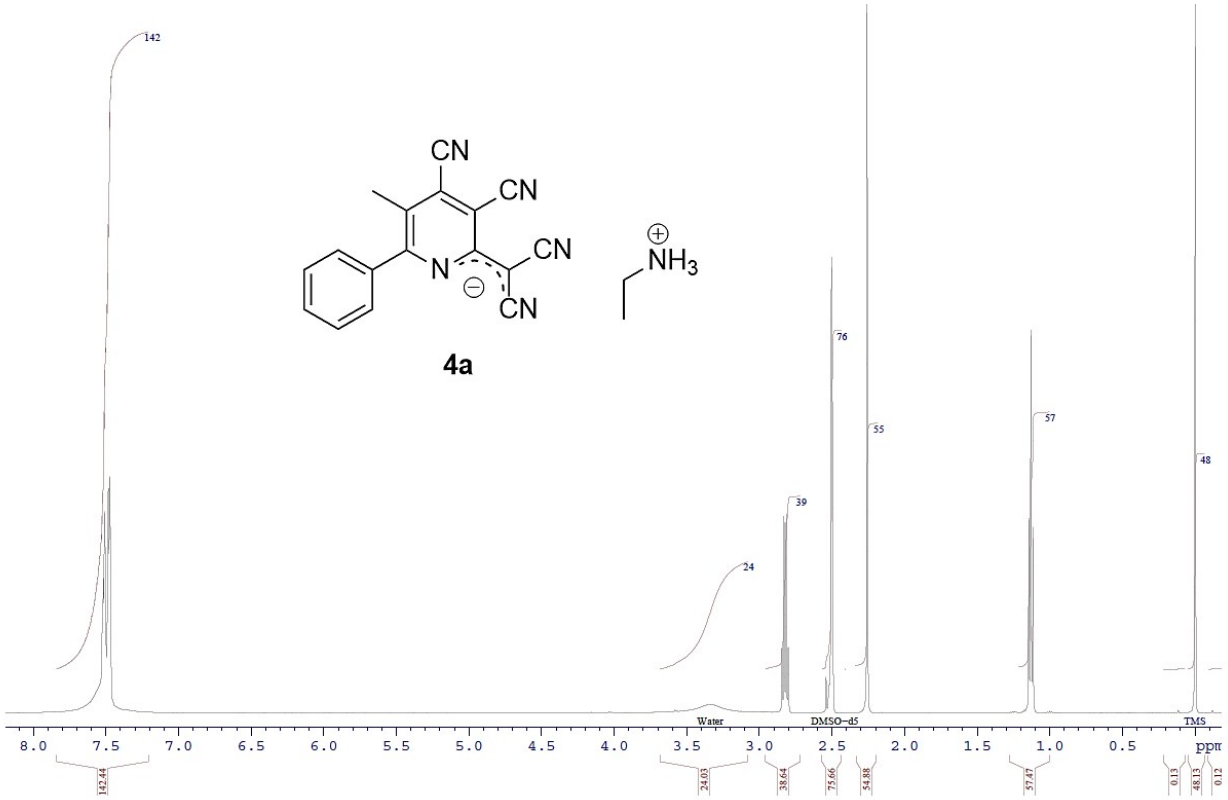

Figure S11 ^{1}H NMR-spectrum of **4a** (500.13 MHz, DMSO−d_6)

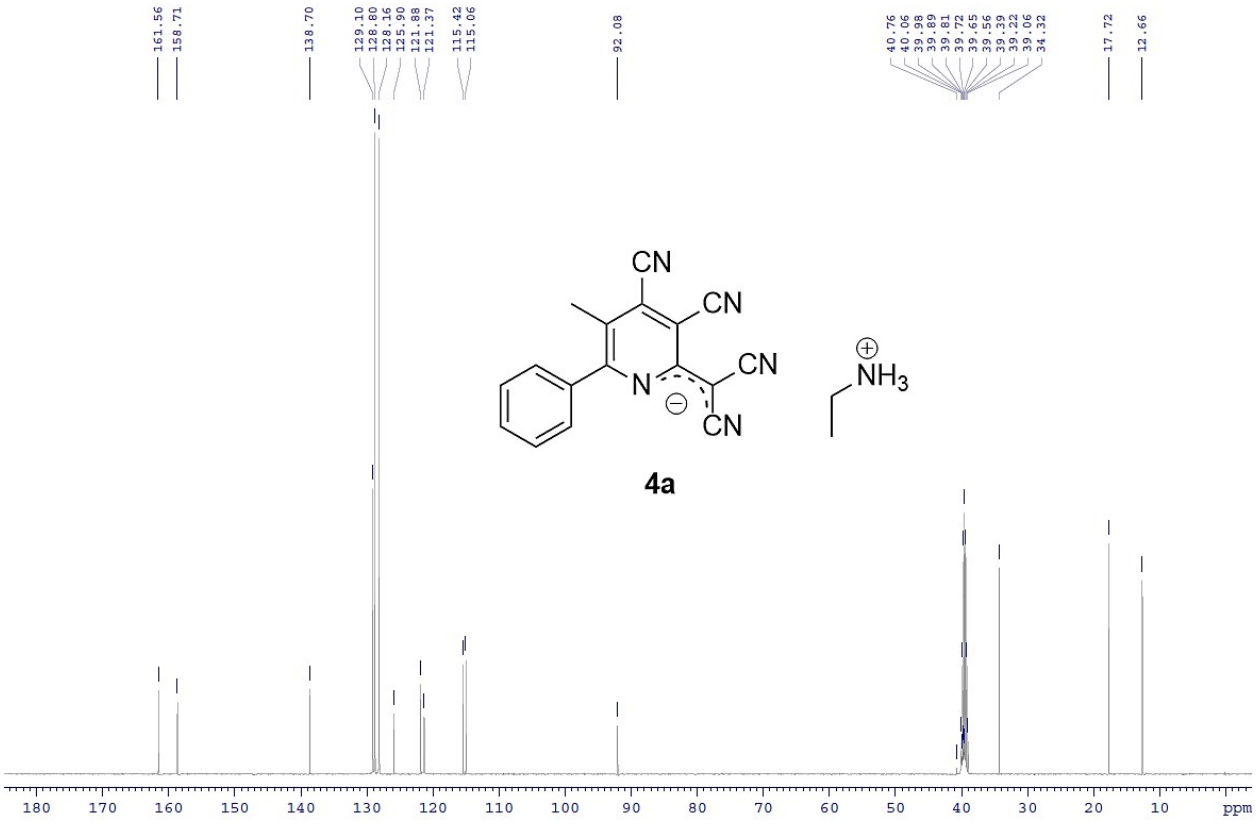

Figure S12 ^{13}C NMR-spectrum of **4a** (150.90 MHz, DMSO−d_6)

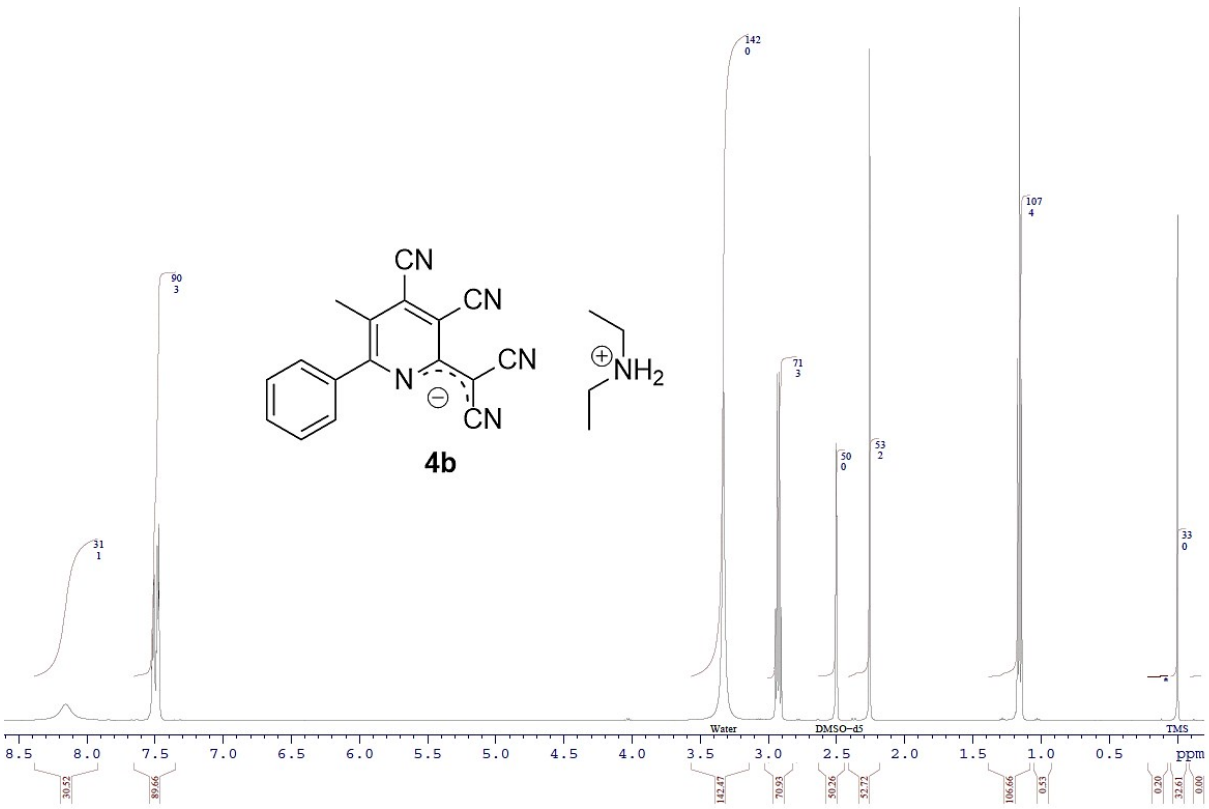

Figure S13 ^{1}H NMR-spectrum of **4b** (500.13 MHz, DMSO−d_6)

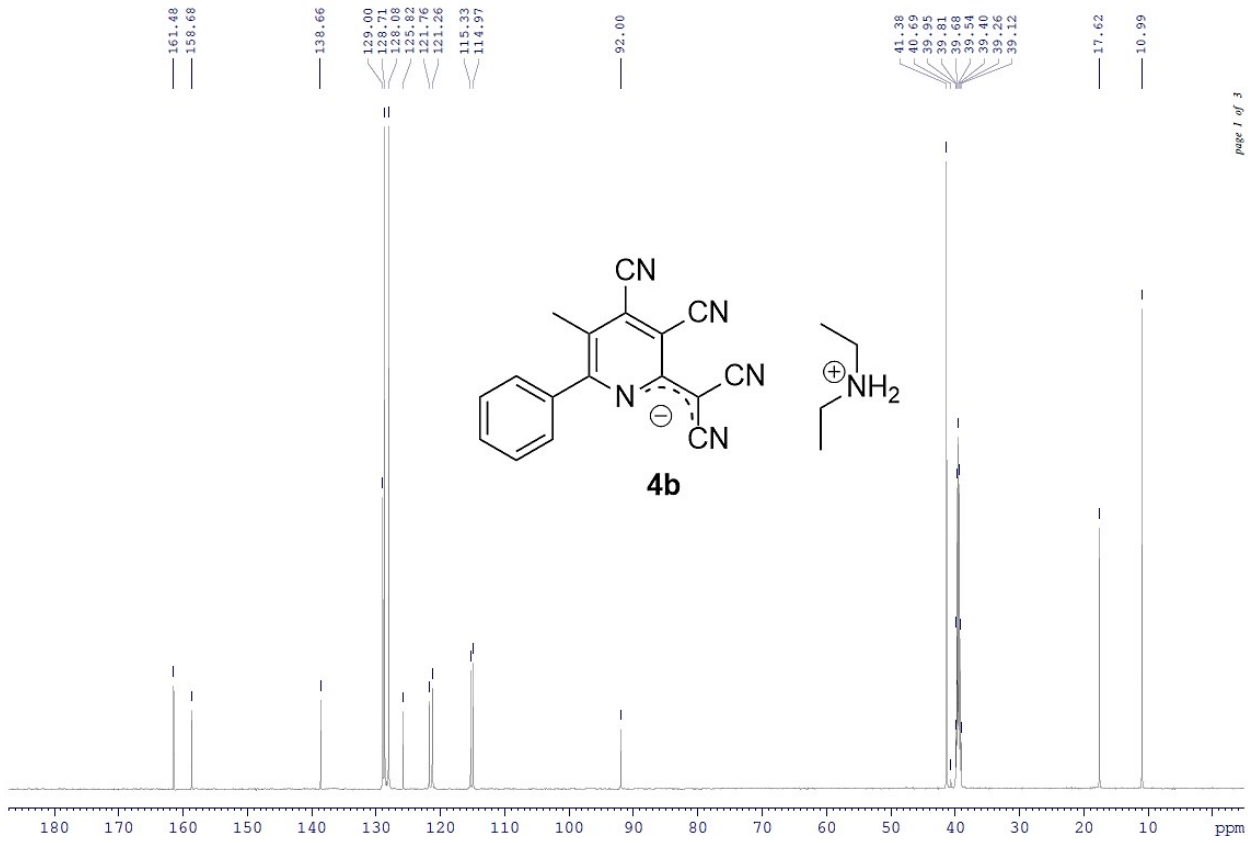

Figure S14 ^{13}C NMR-spectrum of **4b** (150.90 MHz, DMSO−d_6)

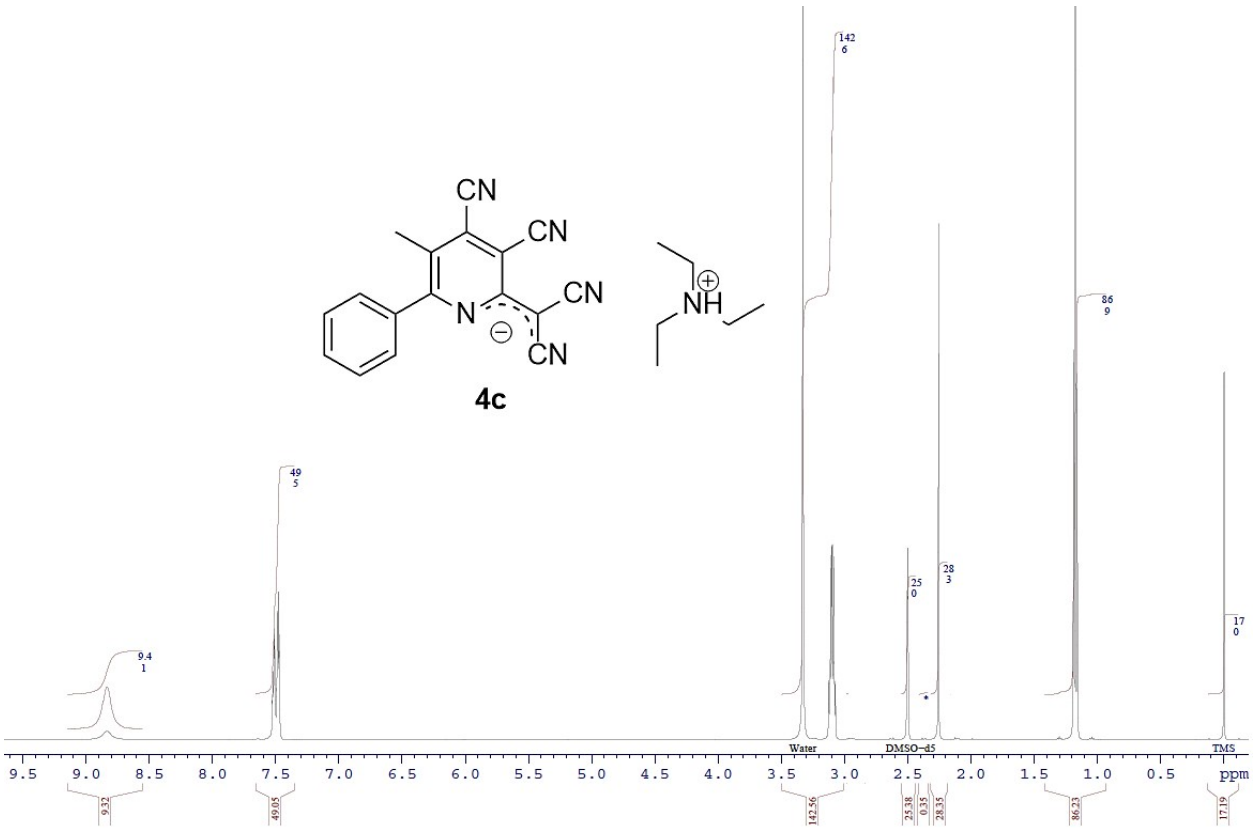

Figure S15 ^{1}H NMR-spectrum of **4c** (500.13 MHz, DMSO−d_6)

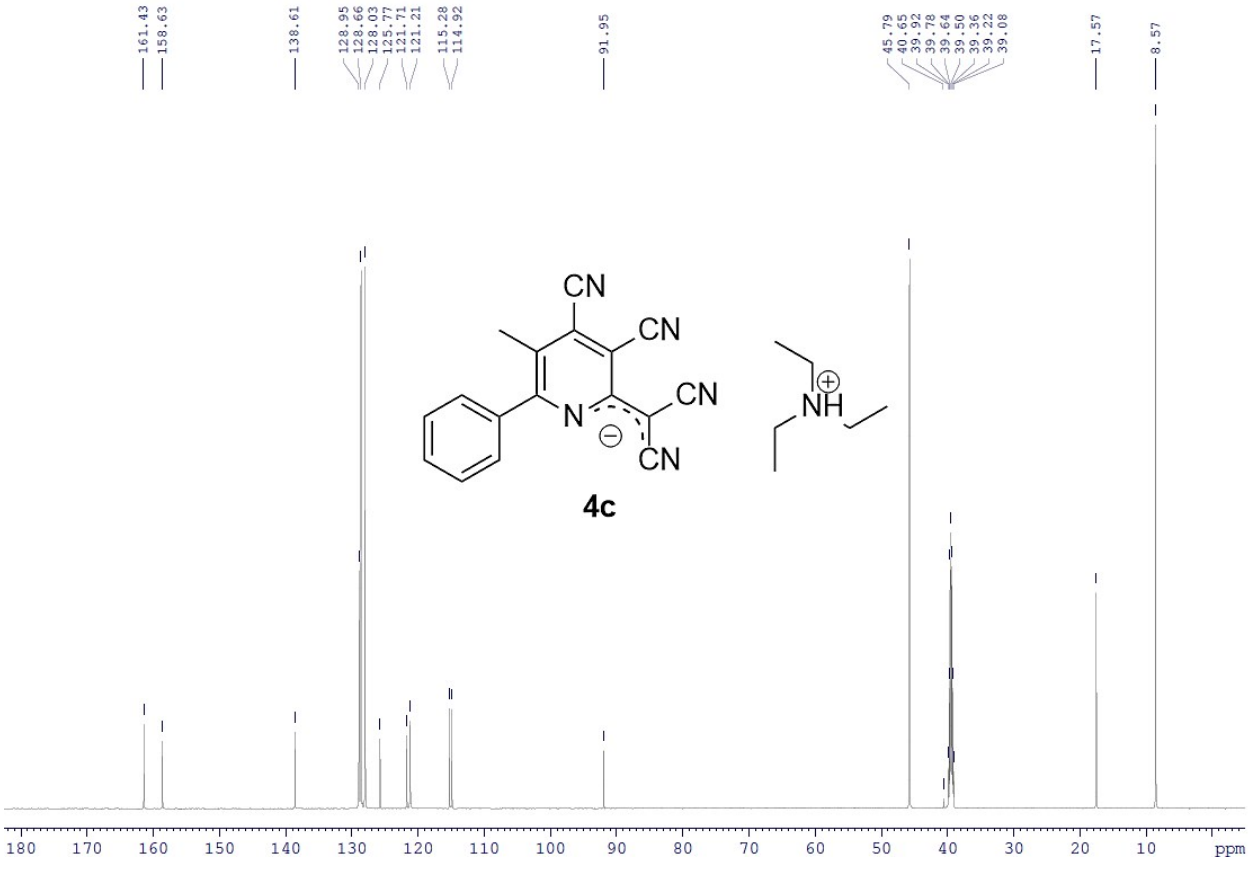

Figure S16 ^{13}C NMR-spectrum of **4c** (125.76 MHz, DMSO−d_6)

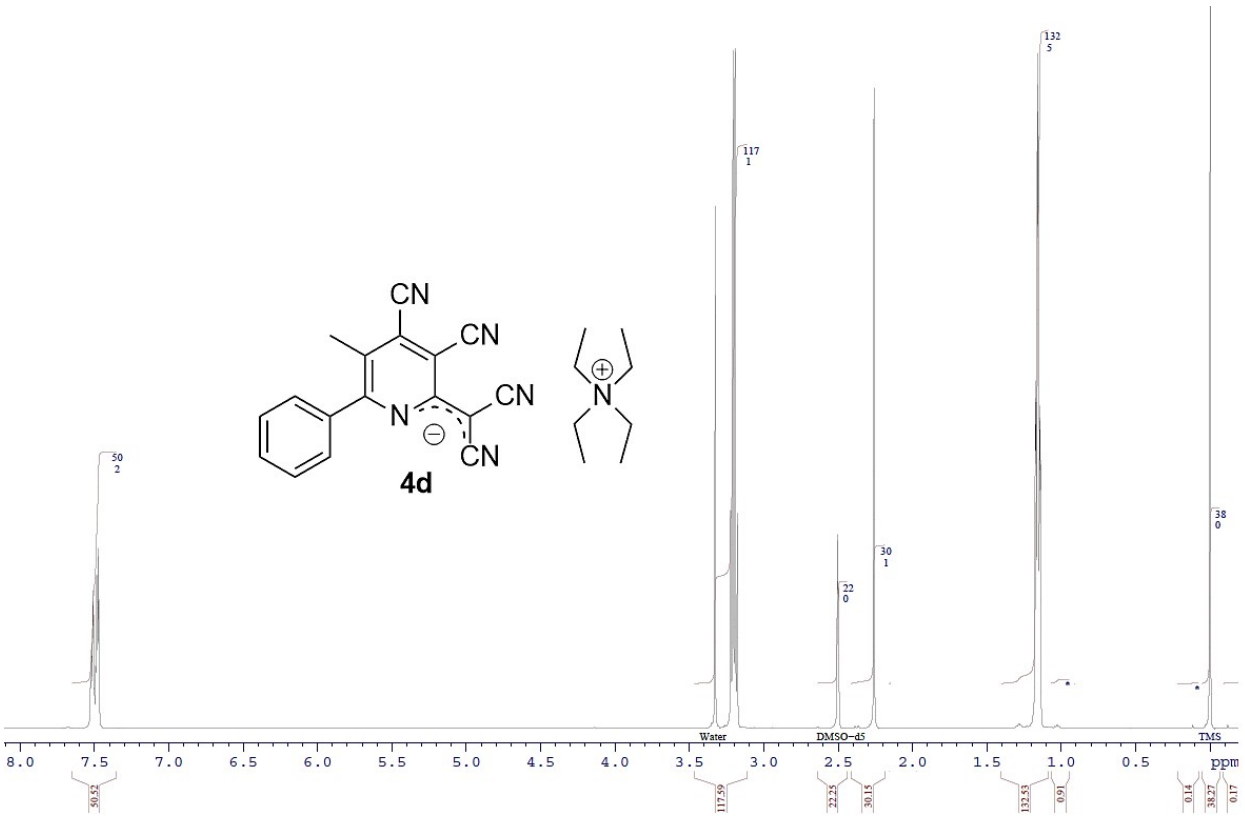

Figure S17 ^{1}H NMR-spectrum of **4d** (500.13 MHz, DMSO−d_6)

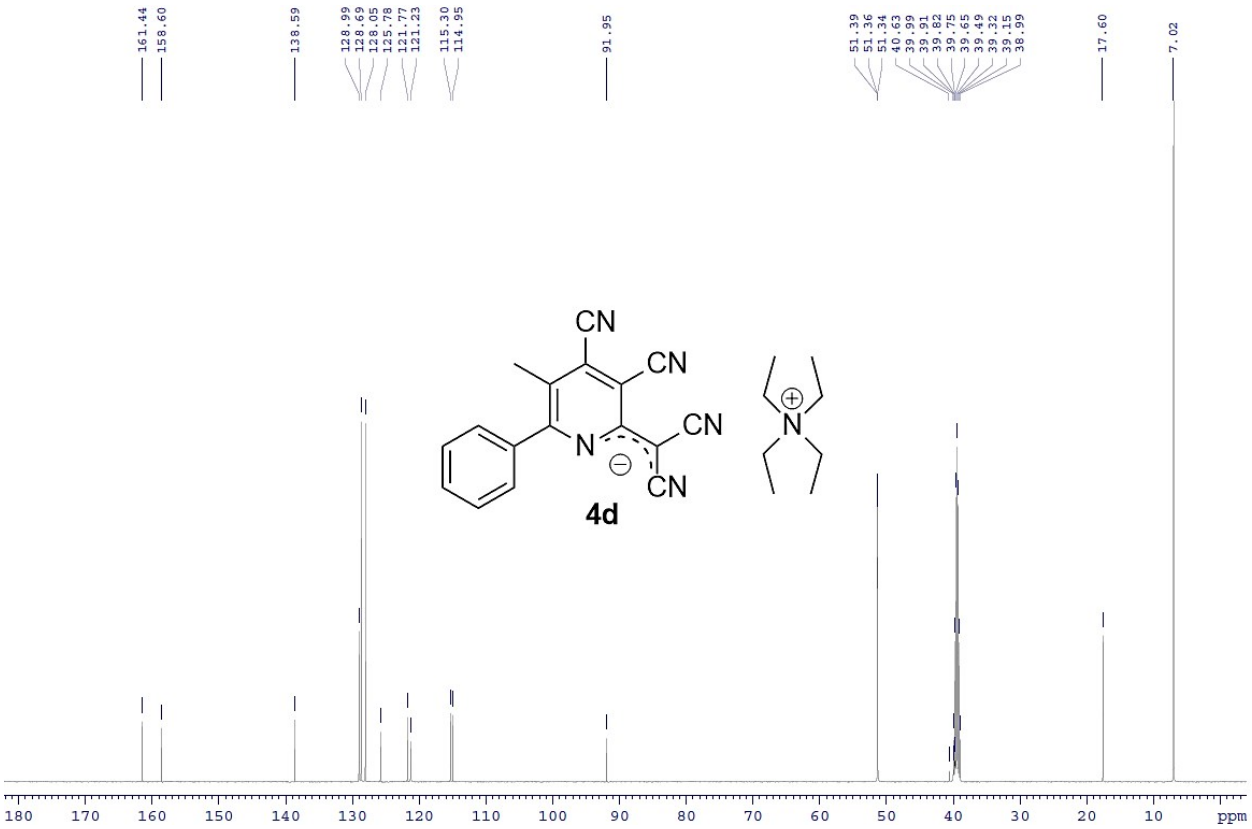

Figure S18 ^{13}C NMR-spectrum of **4d** (125.76MHz, DMSO−d_6)

4. Determination of gaseous amines

Determination of gaseous ethylamine, diethylamine and triethylamine

To 1 g of pure KBr 0.1 g of solid TCPy **3** was added. The mixture was thoroughly grinded using a mortar and pestle. Then, 0.2 g of the resulting homogeneous powder was placed in a glass tube with diameter of 5 mm and a wall thickness of 1 mm. A cotton wool was placed on both sides to hold the mixture inside the tube. The prepared test stick (Fig. S19) was held about 1 cm above the container with corresponding amine. Due to the diffusion of the amine vapor through the tube, the filler was stained and acquired the appropriate fluorescence. Then, the content of the test stick was poured out and solid-state emission spectra were registered (Fig. S20).

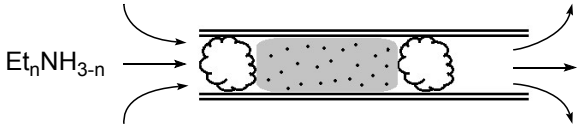

Fig. S19 Schematic illustration of the developed test stick

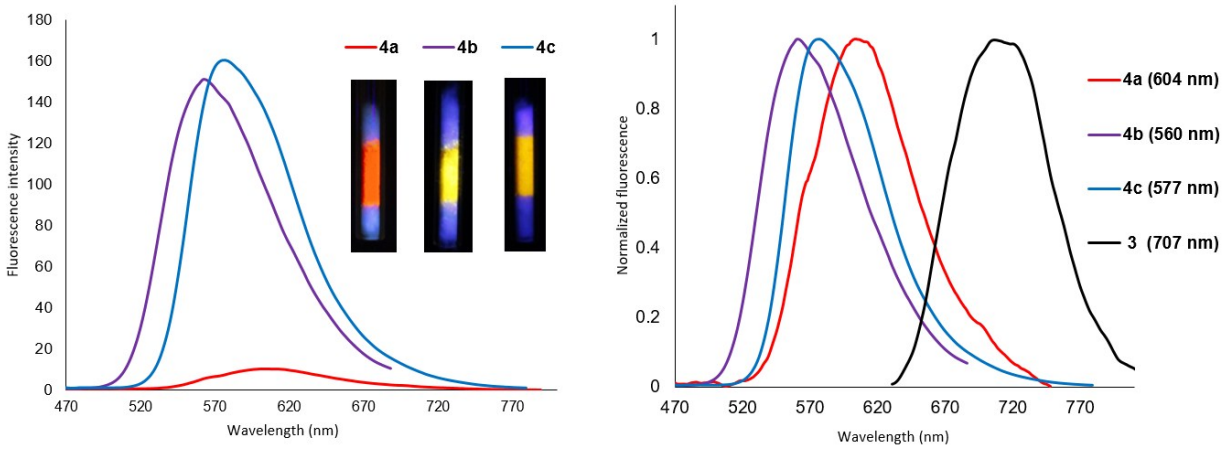

Fig. S20 Emission (left) and normalized emission (right) spectra of the compounds **4a-c** formed on the KBr and compound **3** as control

Note: A slight shift of the emission maxima for the resulting mixtures is caused by the solvent-free formation of compounds **4a-c** on a surface of KBr. For the full crystallographic characterization and photoluminescence studies of ethylammonium salts **4a-c** described in the paper the single crystals were carefully grown by slow evaporation of the solvent, therefore the molecular packing could slightly differs. To validate the that the mixture formed during the gaseous amine detection is indeed the compounds **4** the resulting mixtures were washed with water to remove KBr and then NMR spectra were registered.

References

1. G.M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112.
2. O.V. Ershov, M.Y. Ievlev, M.Y. Belikov, K.V. Lipin, A.I. Naydenova, V. A. Tafeenko, *RSC Adv*. **2016**, *6*, 82227–82232.
3. S.S. Chunikhin, O.V. Ershov, M.Y. Ievlev, M.Y. Belikov, V.A. Tafeenko, *Dyes Pigm*. **2018**, *156*, 357–368.