Supporting Information

Alkali Metals salts of a Tetracyanopyridine (TCPy) Derivative: Structure Characterization and Luminescence Properties

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1. Photoluminescence spectra

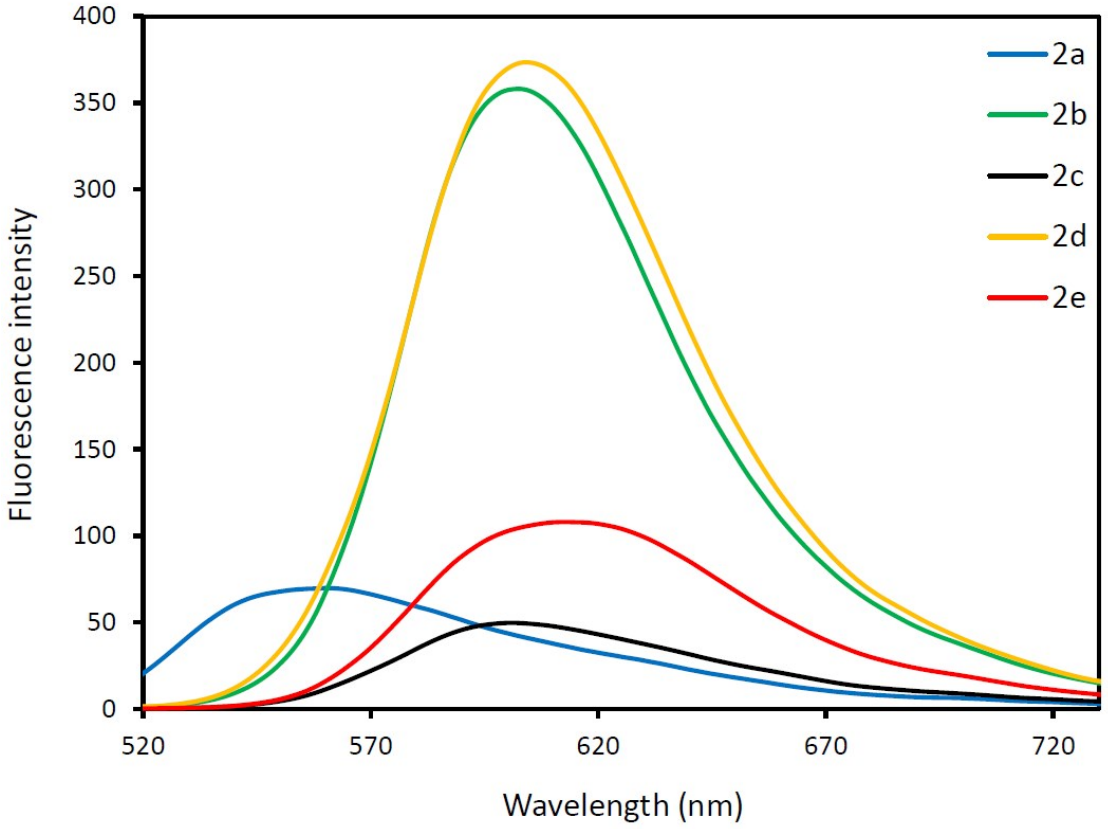

Figure S1 Solid-state emission of compounds **2a-e** (excitation wavelength 350 nm).

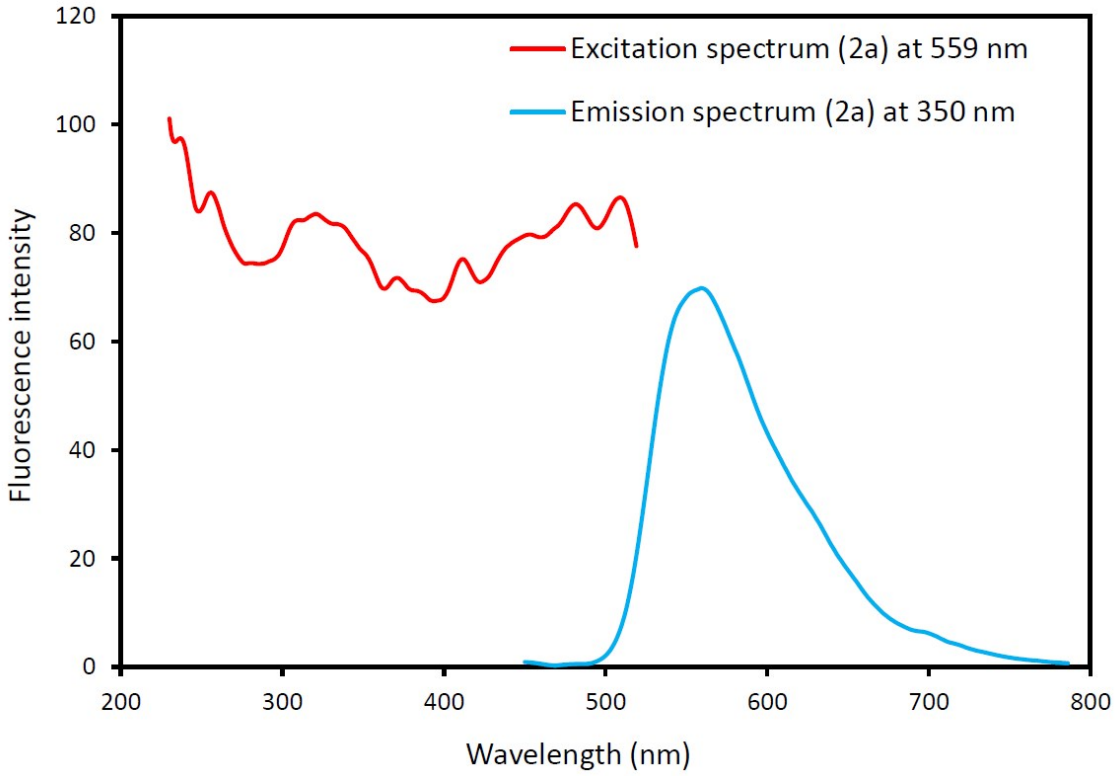

Figure S2 Excitation and emission spectra of compound **2a** in the solid state.

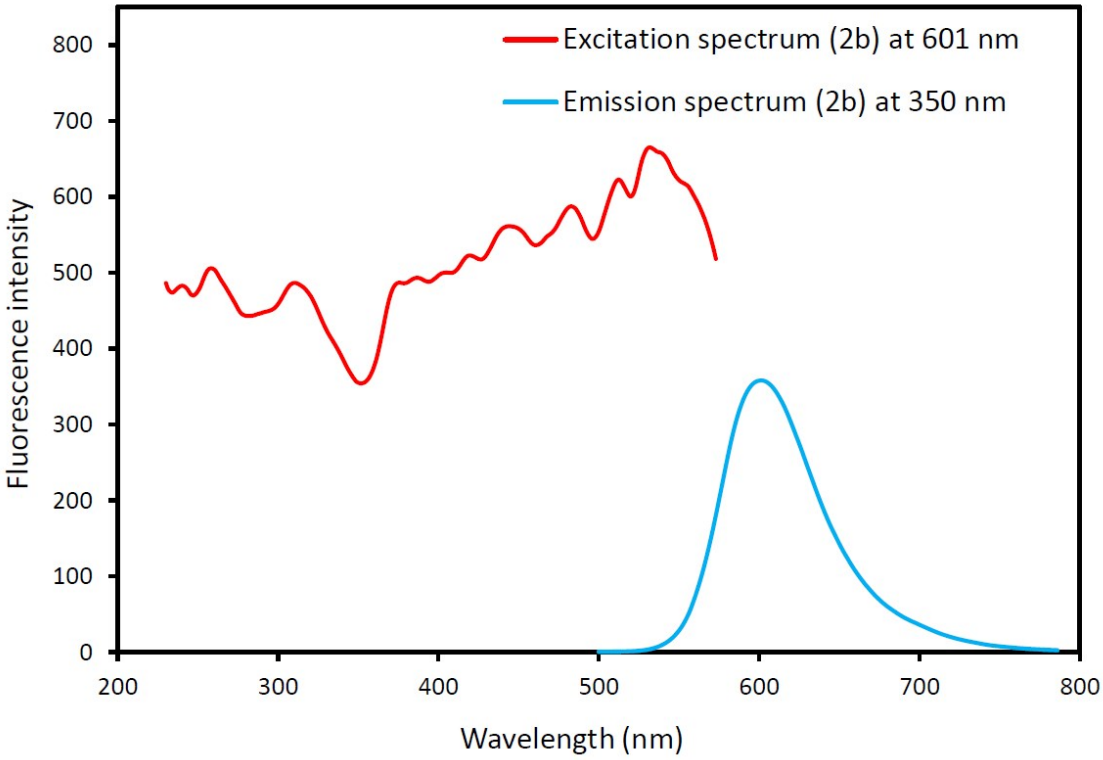

Figure S3 Excitation and emission spectra of compound **2b** in the solid state.

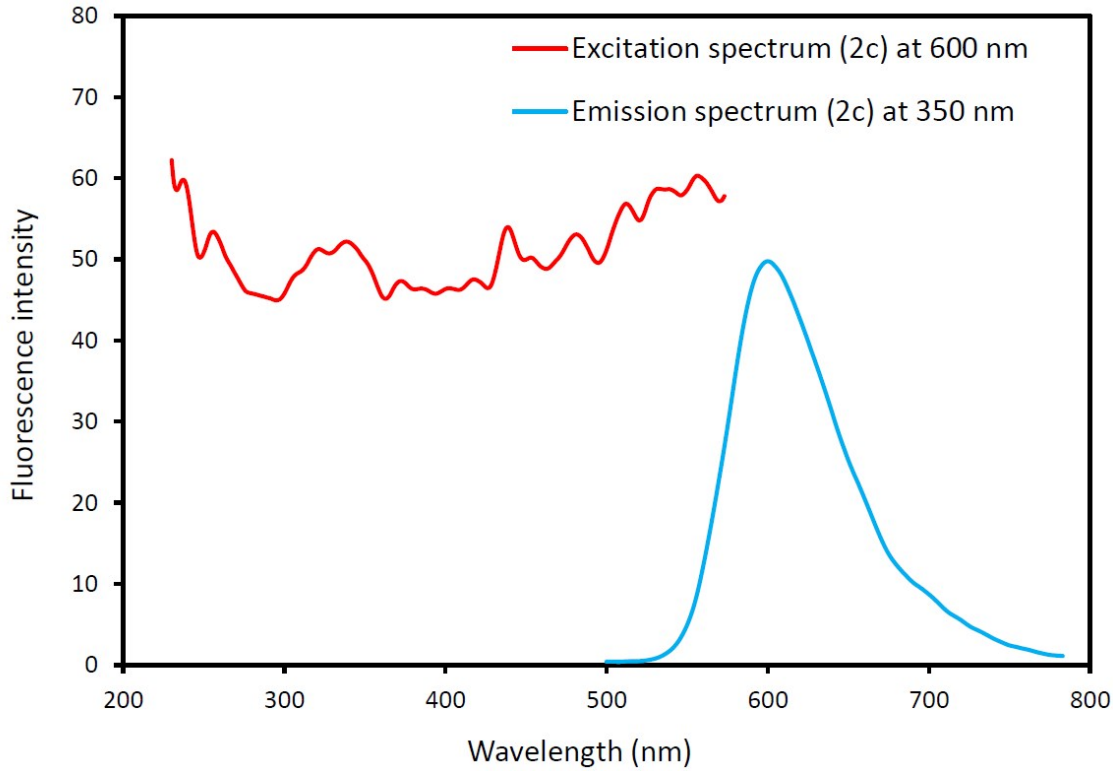

Figure S4 Excitation and emission spectra of compound **2c** in the solid state.

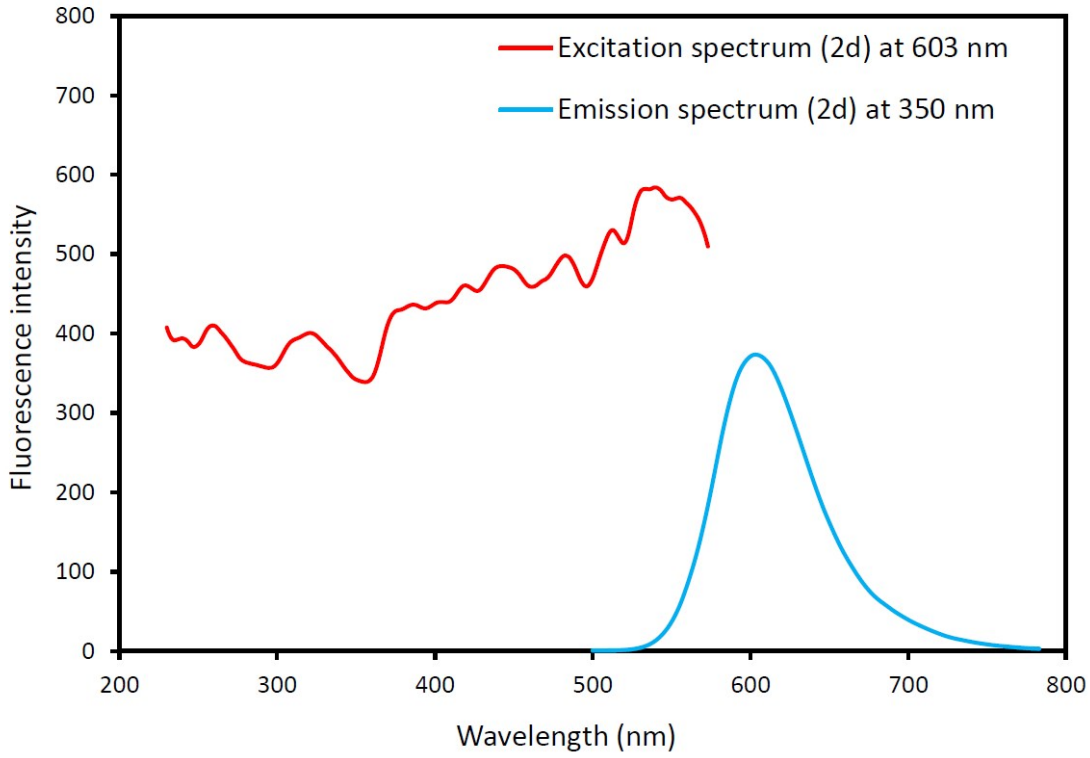

Figure S5 Excitation and emission spectra of compound **2d** in the solid state.

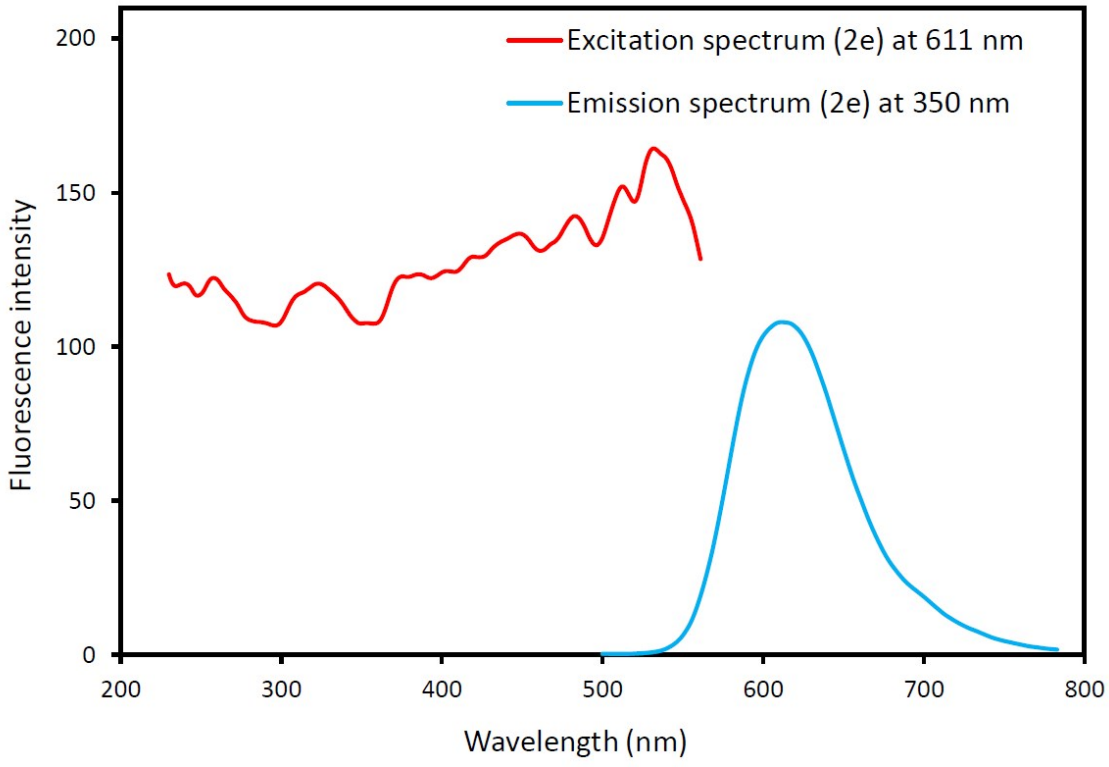

Figure S6 Excitation and emission spectra of compound **2e** in the solid state.

2. Absorption spectra

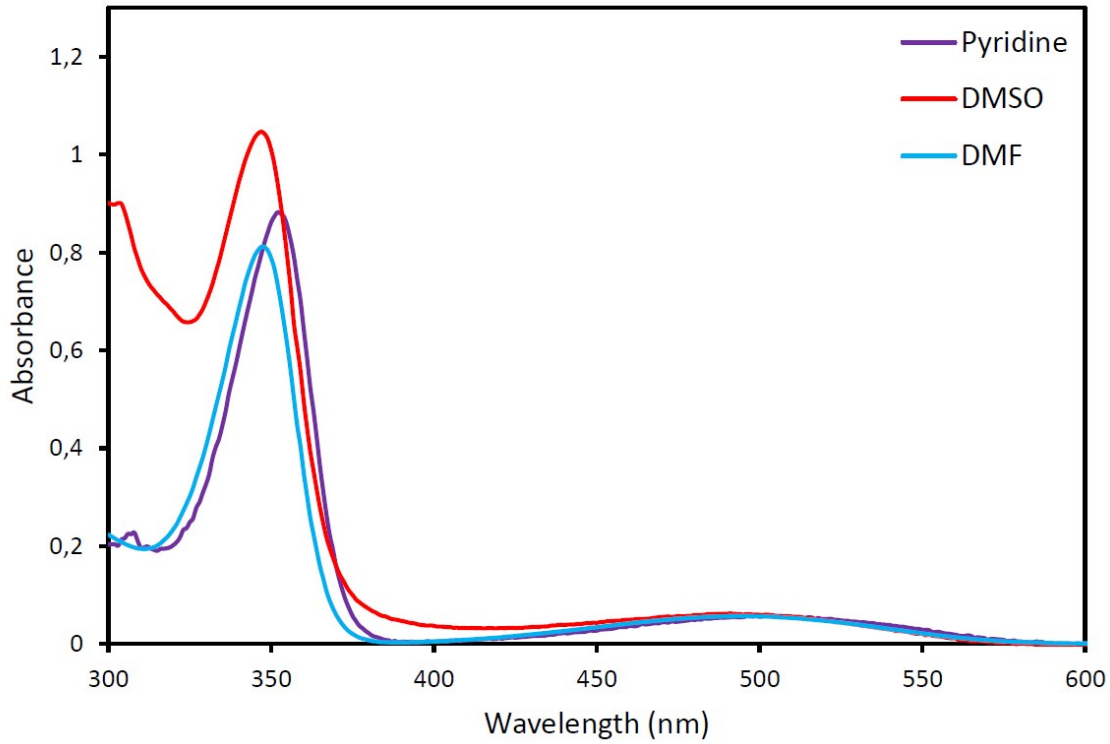

Figure S7 Absorption spectra of compound **2a** in different solvents.

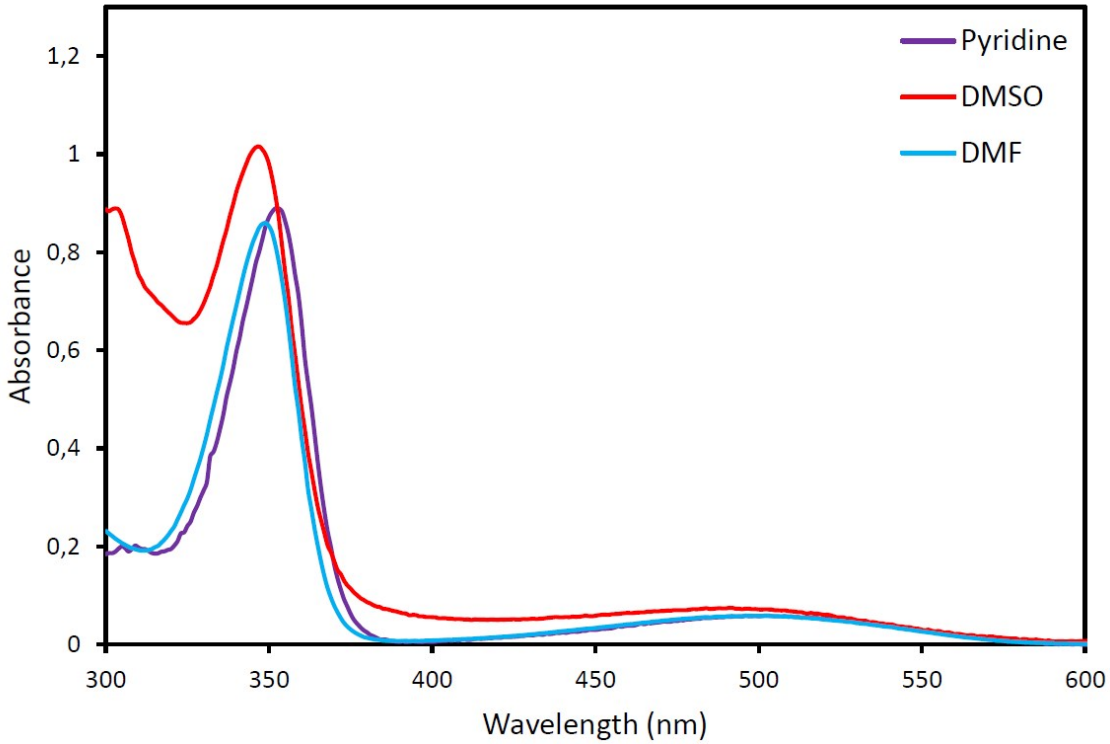

Figure S8 Absorption spectra of compound **2b** in different solvents.

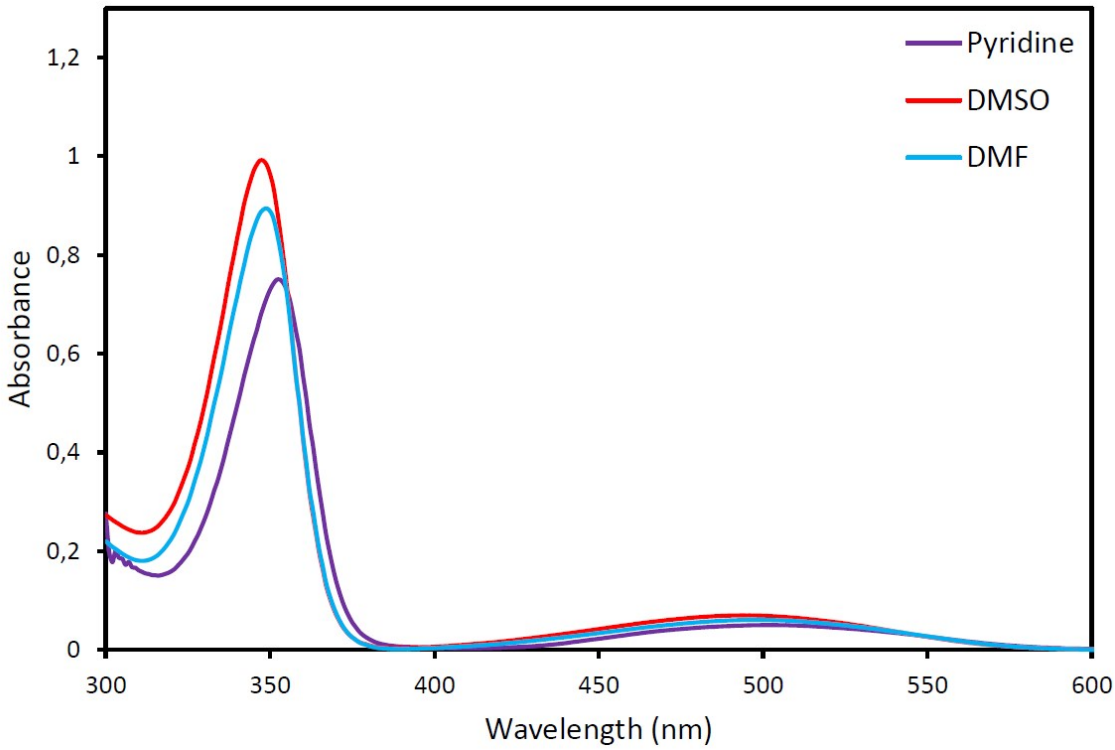

Figure S9 Absorption spectra of compound **2c** in different solvents.

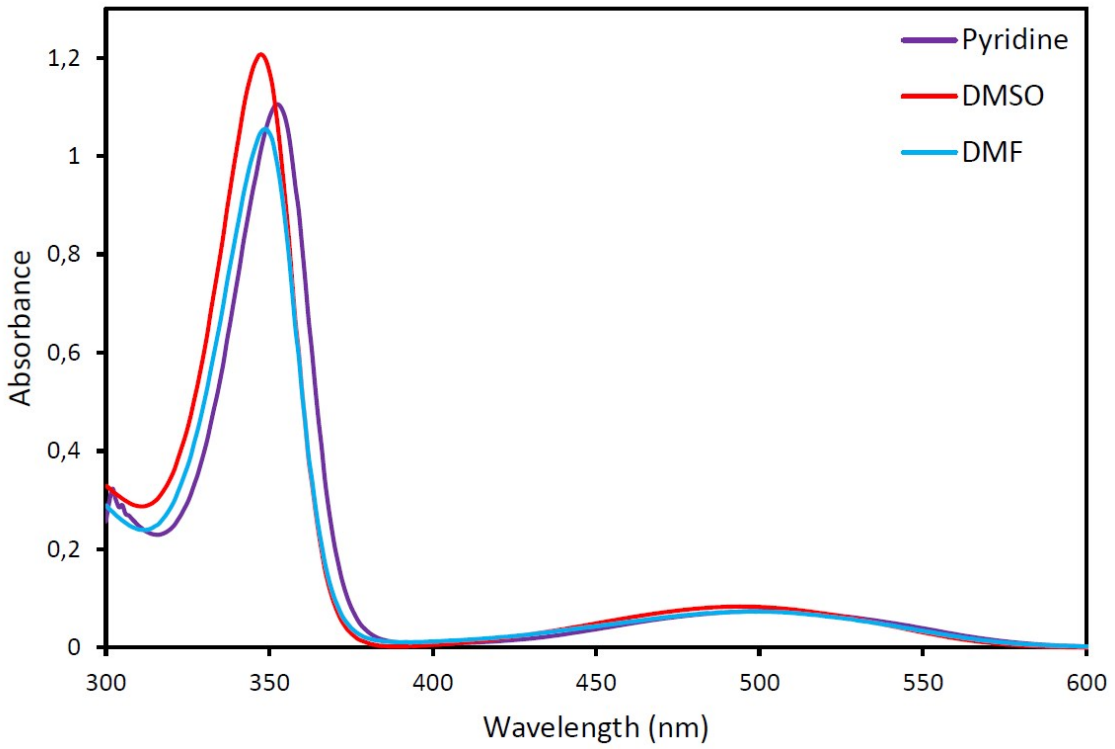

Figure S10 Absorption spectra of compound **2d** in different solvents.

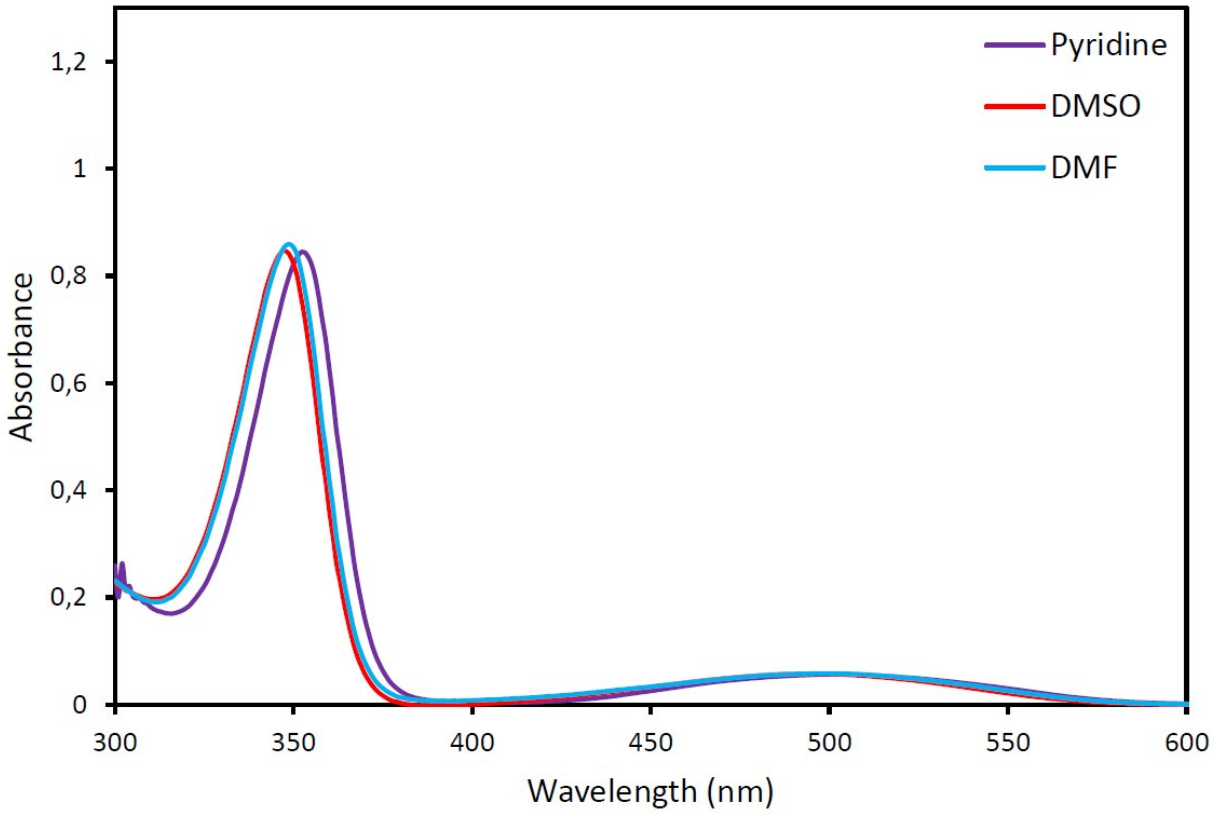

Figure S11 Absorption spectra of compound **2e** in different solvents.

3. 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.

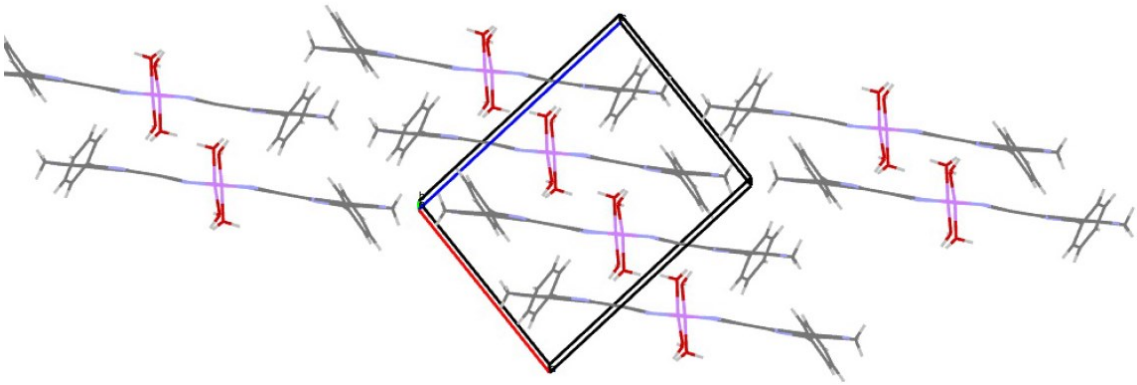

Figure S12 Layers forming a 3D crystal structure of compound **2a**.

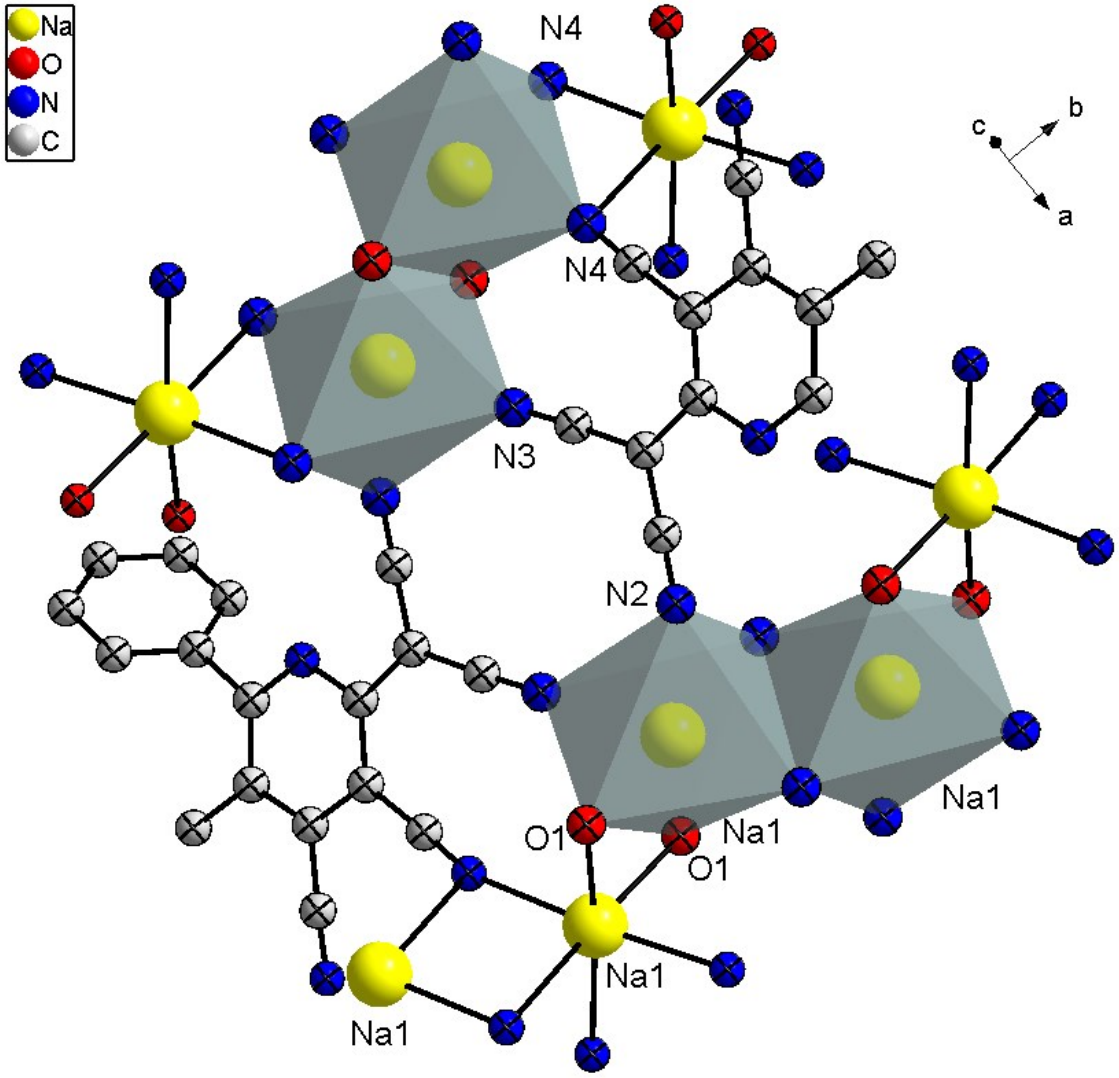

Figure S13 2D layer of crystal **2b**.

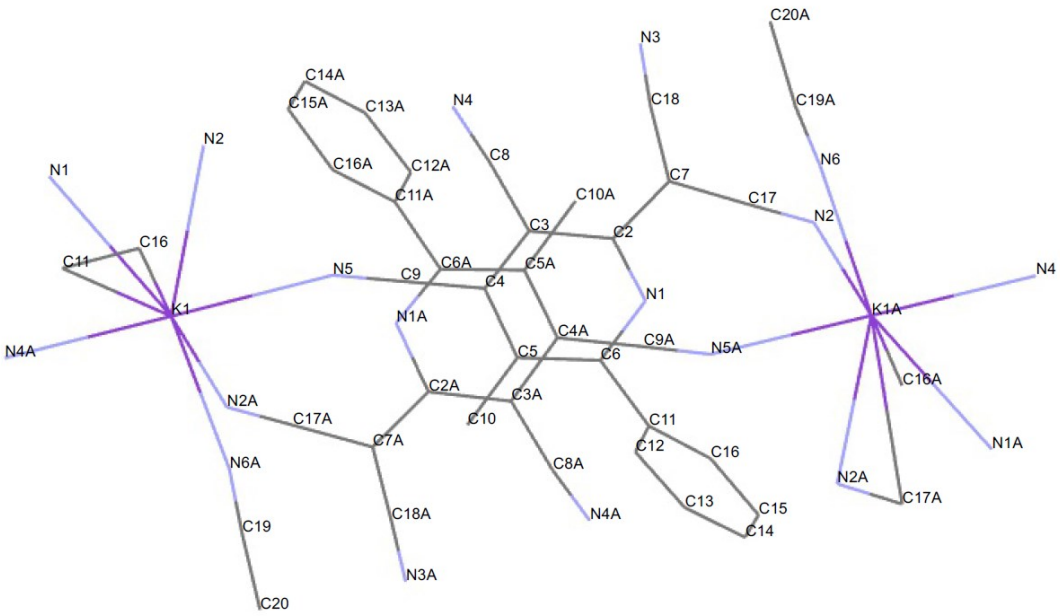

Figure S14 The building block of the crystal structure **2c**.

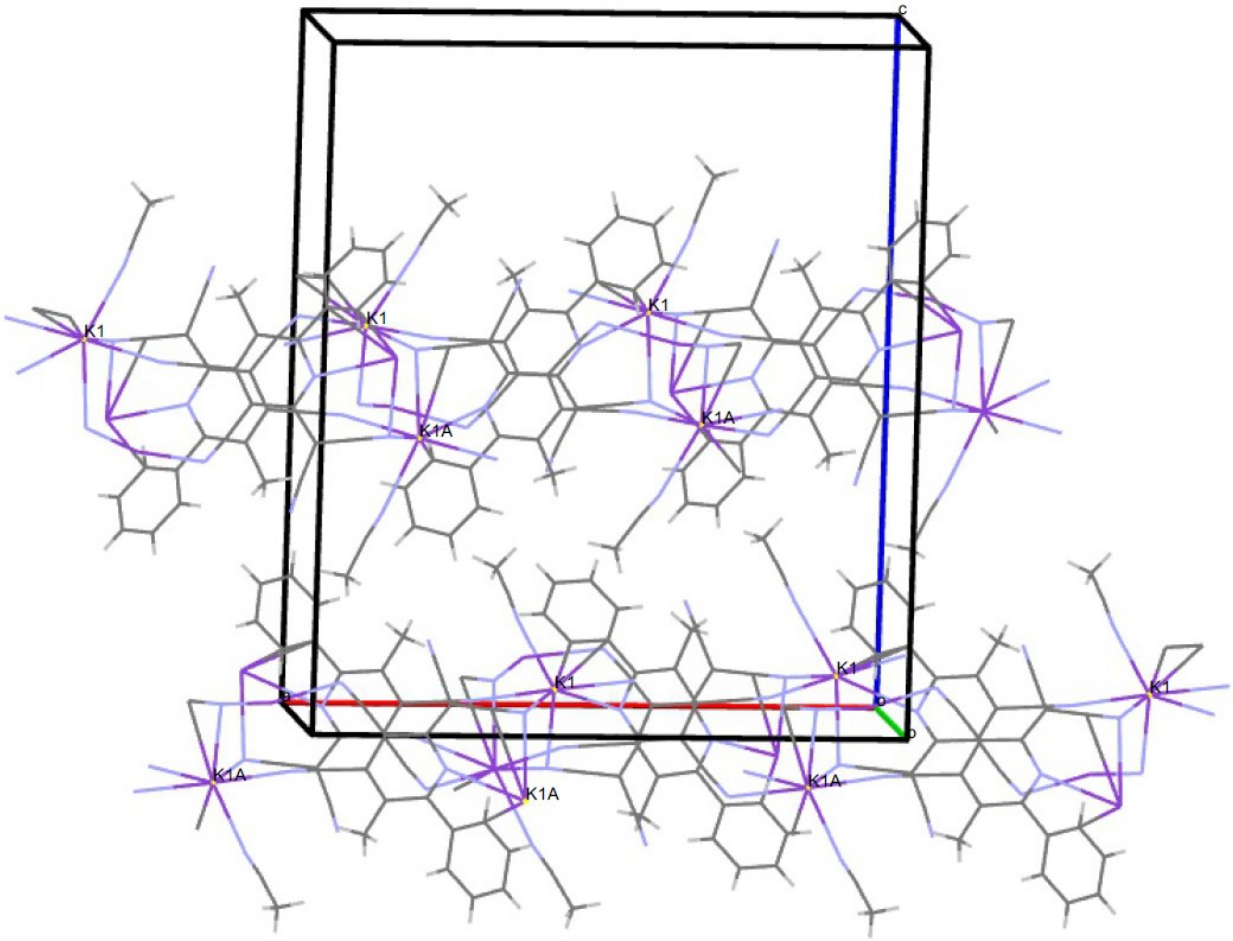

Figure S15 Two layers of compound **2c** connected with each other by weak van der Waals interactions.

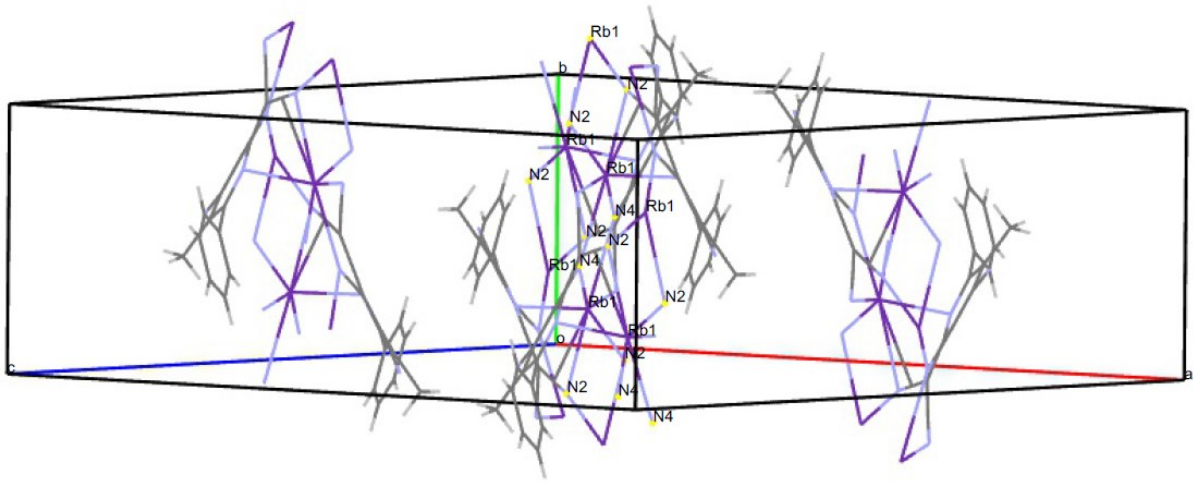

Figure S16 The layers of compound **2d** connected with each other by weak van der Waals interactions.

Table S1 Hydrogen bonds for **2a**, **2b** and **2e** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
2a				
O(1)-H(20)...O(2A)[1]	0.860(10)	2.12(2)	2.872(3)	146(3)
O(1)-H(21)...N(4A)[2]	0.865(10)	2.112(16)	2.922(4)	156(3)
O(1A)-H(20A)...O(2)[3]	0.861(10)	2.086(17)	2.879(3)	153(3)
O(1A)-H(21A)...N(4)[4]	0.866(10)	2.102(16)	2.923(3)	158(3)
O(2)-H(30)...O(1A)[4]	0.860(10)	2.165(11)	3.019(3)	172(3)
O(2)-H(31)...N(1)[4]	0.861(10)	2.444(13)	3.288(3)	167(3)
O(2A)-H(30A)...O(1)[2]	0.859(10)	2.416(13)	3.252(4)	164(3)
O(2A)-H(30A)...N(2A)[2]	0.859(10)	2.59(3)	3.108(3)	120(2)
O(2A)-H(31A)...N(1A)[2]	0.856(10)	2.222(11)	3.073(3)	173(3)
Symmetry transformations used to generate equivalent atoms: (1) x,y-1,z; (2) -x+1,-y+1,-z+1; (3) x,y+1,z; (4) -x+2,-y+1,-z+1				
2b				
O(1)-H(10)...N(5)[1]	0.89(3)	2.10(3)	2.949(2)	160(2)
O(1)-H(11)...N(2)[2]	0.85(3)	2.63(3)	3.342(2)	142(3)
Symmetry transformations used to generate equivalent atoms: (1) x+1/2,y-3/2,z; (2) x,y-1,z				
2e				
O1-H1…N3	0.914	1.991	2.895	169.35

4. **Quantum chemical calculations**

Table S2 Cartesian atomic coordinates (Å) for the TCPy anion (ground state) optimized in non-polar medium

Atom	Charge	X	Y	Z
N1	7.0	10.0843805070	7.0290508297	10.1046487160
C2	6.0	9.8301693709	5.7317538039	9.8278693458
C3	6.0	10.5055810183	4.7303545104	10.5886369859
C4	6.0	11.5412992705	5.1462051354	11.4450644386
C5	6.0	11.8631981196	6.4904892576	11.6358266024
C6	6.0	11.0112246471	7.4033275742	10.9675123326
C7	6.0	8.8886908949	5.4890608015	8.7909972714
C8	6.0	10.1664519017	3.3543369409	10.5609197229
C9	6.0	12.2929093235	4.1589158400	12.1575355166
C10	6.0	13.0494365310	6.8847079081	12.4670348626
C11	6.0	11.1086098183	8.8749809009	11.1578332670
C12	6.0	11.3294320685	9.4546462048	12.4097895399
C13	6.0	11.3669337019	10.8368216173	12.5525427494
C14	6.0	11.1919568153	11.6587536162	11.4453018019
C15	6.0	10.9595591008	11.0905986647	10.1963025148
C16	6.0	10.9086283754	9.7115112887	10.0553718127
C17	6.0	8.2205298969	6.5836271759	8.2019803190
C18	6.0	8.6354308956	4.2328768606	8.2112413182
N19	7.0	7.6487952674	7.4536877313	7.6901065975
N20	7.0	8.4144459377	3.2262119197	7.6772671453
N21	7.0	9.9136511482	2.2272848117	10.6122290326
N22	7.0	12.9183584667	3.3902026550	12.7482027403
H23	1.0	12.8127318031	6.9261627553	13.5363968450
H24	1.0	13.4256512922	7.8651296922	12.1730146142
H25	1.0	13.8589275726	6.1603735124	12.3482971756
H26	1.0	11.4406703073	8.8261732589	13.2861266176
H27	1.0	11.5258898422	11.2708687876	13.5344957908
H28	1.0	11.2270484445	12.7378070108	11.5565077945
H29	1.0	10.8101860630	11.7251724600	9.3286841116
H30	1.0	10.6991757027	9.2585074205	9.0933508096

Table S3 Cartesian atomic coordinates (Å) for the TCPy anion (ground state) optimized in polar medium.

Atom	Charge	X	Y	Z
N1	7.0	10.1049640177	7.0316657717	10.0762940226
C2	6.0	9.8579958502	5.7310446098	9.8104931033
C3	6.0	10.5984546839	4.7359152120	10.5046070219
C4	6.0	11.5342750878	5.1585241827	11.4701762395
C5	6.0	11.7579778491	6.5028321265	11.7545606695
C6	6.0	10.9786228745	7.4099234617	10.9948874295
C7	6.0	8.8473628039	5.4819950979	8.8315978890
C8	6.0	10.4924717003	3.3475206733	10.2420413499
C9	6.0	12.2904734864	4.1651578477	12.1684469531
C10	6.0	12.7964380376	6.9211569653	12.7514410729
C11	6.0	11.1078322160	8.8811747123	11.1563080209
C12	6.0	11.0627911547	9.4907817690	12.4122397130
C13	6.0	11.1341433118	10.8742088920	12.5248474380
C14	6.0	11.2687698087	11.6621432441	11.3870782644
C15	6.0	11.3151328869	11.0618890901	10.1320506926
C16	6.0	11.2236203884	9.6818509661	10.0167998467
C17	6.0	8.2493352676	6.5717614952	8.1709214963
C18	6.0	8.3272551742	4.2234392637	8.4929820549
N19	7.0	7.7266735671	7.4339572437	7.5957107242
N20	7.0	7.8431327897	3.2140532554	8.1827588171
N21	7.0	10.4692289296	2.2068709264	10.0552357354

N22	7.0	12.8998987825	3.3697425736	12.7394206189
H23	1.0	12.3799494434	7.0014026938	13.7611623555
H24	1.0	13.2228282978	7.8909013740	12.4926678425
H25	1.0	13.6091186050	6.1931685975	12.7935808089
H26	1.0	10.9416278653	8.8873620446	13.3053983367
H27	1.0	11.0822295024	11.3366802243	13.5049766460
H28	1.0	11.3331836999	12.7416410748	11.4773154267
H29	1.0	11.4191515068	11.6719474078	9.2405991073
H30	1.0	11.2417935594	9.2079048471	9.0416386540

Table S4 Characteristics of electronic transitions calculated for ground-state geometry of the TCPy anion in non-polar medium

STATE#1 ENERGY		2.289663 EV	
OSCILLATOR STRENGTH		0.034869	
LAMBDADIAGNOSTIC		0.451 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	
EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
72	74	0.032375	0.016995
73	74	0.997566	-0.046391
68	75	-0.037482	-0.021552
STATE#2 ENERGY		3.555310 EV	
OSCILLATOR STRENGTH		0.347315	
LAMBDADIAGNOSTIC		0.560 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	
EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
68	74	-0.037238	-0.011585
73	75	-0.996753	0.055882
73	77	-0.018004	-0.032438

Table S5 Characteristics of electronic transitions calculated for ground-state geometry of the TCPy anion in non-polar medium

STATE#1 ENERGY		2.508702 EV	
OSCILLATOR STRENGTH		0.043494	
LAMBDADIAGNOSTIC		0.474 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	
EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
69	74	0.032674	0.025224
73	74	0.996931	-0.045542
68	75	-0.055694	-0.030286
STATE#2 ENERGY		3.826053 EV	
OSCILLATOR STRENGTH		0.436573	
LAMBDADIAGNOSTIC		0.639 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	

EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
68	74	-0.035612	-0.008324
69	74	0.031153	0.008299
73	75	-0.994640	0.064997
73	78	0.051035	-0.007282

Table S6 Cartesian atomic coordinates (Å) for the TCPy anion (excited state) optimized in non-polar medium

Atom	Charge	X	Y	Z
N1	7.0	10.1389884128	7.0063692818	10.0450262293
C2	6.0	9.9286065071	5.7333766952	9.8463285043
C3	6.0	10.5644566190	4.7024070210	10.5529750373
C4	6.0	11.5715105897	5.1133387586	11.5088382025
C5	6.0	11.8019696355	6.4987188529	11.7241653992
C6	6.0	11.0354580551	7.4135881019	11.0167068417
C7	6.0	8.9066352350	5.4778307851	8.7931119545
C8	6.0	10.3167789023	3.3320948286	10.3541917486
C9	6.0	12.3186945481	4.1589304726	12.2139207555
C10	6.0	12.9022878434	6.8819297875	12.6685596256
C11	6.0	11.1141327842	8.8749390188	11.1723192128
C12	6.0	11.3361573339	9.5070219075	12.4058358465
C13	6.0	11.3675338991	10.8918731697	12.5068731988
C14	6.0	11.1700990705	11.6863993778	11.3821871525
C15	6.0	10.9222538191	11.0748745606	10.1556487841
C16	6.0	10.8847220911	9.6929725936	10.0532601636
C17	6.0	8.3184116282	6.5871698691	8.1682530592
C18	6.0	8.4301788035	4.2417988195	8.3502911811
N19	7.0	7.7939921242	7.4588190506	7.6093839617
N20	7.0	7.9762879851	3.2624068387	7.9206970173
N21	7.0	10.1557727866	2.1884522168	10.2409306140
N22	7.0	12.9443237813	3.3745302213	12.8055918185
H23	1.0	12.5609909632	6.8571888078	13.7097969335
H24	1.0	13.2840953299	7.8808336701	12.4595180579
H25	1.0	13.7250730282	6.1667796470	12.5926593413
H26	1.0	11.4415875330	8.9131855706	13.3058649246
H27	1.0	11.5299472399	11.3520657845	13.4767917376
H28	1.0	11.1927021386	12.7683559701	11.4632098038
H29	1.0	10.7507316007	11.6814043744	9.2715121236
H30	1.0	10.6657236428	9.2164605997	9.1051087657

Table S7 Cartesian atomic coordinates (Å) for the TCPy anion (excited state) optimized in non-polar medium

Atom	Charge	X	Y	Z
N1	7.0	10.1224709406	7.0184060470	10.0326491221
C2	6.0	9.9262668059	5.7370909769	9.8230511933
C3	6.0	10.5990739701	4.7079655608	10.5082301975
C4	6.0	11.5904776120	5.1217267246	11.4783132689
C5	6.0	11.7913071090	6.5118616362	11.7125504340
C6	6.0	11.0259752013	7.4180341117	10.9936340666
C7	6.0	8.8831759837	5.4724392315	8.8171015831
C8	6.0	10.3578863006	3.3385516844	10.3152407261
C9	6.0	12.3348880310	4.1675732616	12.1803239220
C10	6.0	12.8489774688	6.9141202624	12.6924424465
C11	6.0	11.1220044117	8.8832681947	11.1559263228
C12	6.0	11.1010730127	9.4983461608	12.4137836962
C13	6.0	11.1429570022	10.8828930304	12.5298806256
C14	6.0	11.2097547341	11.6810560777	11.3929638351

C15	6.0	11.2272858339	11.0821561937	10.1354836164
C16	6.0	11.1750659364	9.7005655756	10.0188786678
C17	6.0	8.2442605424	6.5733751346	8.2218373181
C18	6.0	8.4094457557	4.2251733815	8.3943649292
N19	7.0	7.6787816025	7.4369892678	7.6948066961
N20	7.0	7.9626032081	3.2309759910	7.9968070511
N21	7.0	10.2059944397	2.1915199651	10.2090153314
N22	7.0	12.9504297711	3.3651564458	12.7600779553
H23	1.0	12.5011430873	6.7831136236	13.7236742583
H24	1.0	13.1461762902	7.9539265436	12.5653414865
H25	1.0	13.7322890939	6.2798262804	12.5748699518
H26	1.0	11.0166236019	8.8902988134	13.3083784845
H27	1.0	11.1118739609	11.3394456093	13.5141688562
H28	1.0	11.2414238539	12.7618452228	11.4846186923
H29	1.0	11.2782930143	11.6964639250	9.2418579976
H30	1.0	11.1702640774	9.2329330186	9.0401416565

Table S8 Characteristics of electronic transitions calculated for excited-state geometry of the TCPy anion in non-polar medium

STATE#1 ENERGY		1.629363 EV	
OSCILLATOR STRENGTH		0.014458	
LAMBDADIAGNOSTIC		0.376 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	
EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
73	74	0.999325	-0.044406
STATE#2 ENERGY		3.238859 EV	
OSCILLATOR STRENGTH		0.246897	
LAMBDADIAGNOSTIC		0.457 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	
EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
68	74	-0.035612	-0.008324
69	74	0.031153	0.008299
73	75	-0.994640	0.064997
73	78	0.051035	-0.007282
STATE#3 ENERGY		3.656220 EV	
OSCILLATOR STRENGTH		0.172083	
LAMBDADIAGNOSTIC		0.534 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	
EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
67	74	0.135631	-0.006816
69	74	-0.067596	-0.007302
70	74	-0.521031	0.011458
71	74	0.441601	-0.007000
72	74	0.704795	-0.030861
69	75	0.036044	0.011235
73	77	-0.040381	-0.000062
70	91	0.035883	-0.006472

Table S9 Characteristics of electronic transitions calculated for excited-state geometry of the TCPy anion in polar medium

STATE#1 ENERGY		2.005308 EV	
OSCILLATOR STRENGTH		0.024976	
LAMBDADIAGNOSTIC		0.421 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	
EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
73	74	-0.998258	0.043575
69	75	-0.039100	-0.024591
STATE#2 ENERGY		3.654885 EV	
OSCILLATOR STRENGTH		0.301212	
LAMBDADIAGNOSTIC		0.524 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	
EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
68	74	-0.051731	0.005408
69	74	0.047404	0.021496
70	74	-0.202984	0.003300
71	74	0.103407	0.000088
72	74	0.957100	-0.031074
68	75	0.036762	0.015441
69	75	-0.035382	-0.008211
73	75	-0.119511	0.009279
73	78	0.040413	-0.002064
STATE#3 ENERGY		3.675697 EV	
OSCILLATOR STRENGTH		0.306740	
LAMBDADIAGNOSTIC		0.558 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	
EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
69	74	-0.042086	-0.007329
72	74	0.122414	-0.001192
72	75	0.036561	0.007627
73	75	0.981187	-0.046684
73	78	-0.105998	0.013807

Table S10 Cartesian atomic coordinates (Å) for Li-1 model (two Li^+ cations positioned at the dicyanomethylene group of the TCPy anion (excited state)

Atom	Charge	X	Y	Z
N1	7.0	10.1224641337	7.0184091821	10.0326557809
C2	6.0	9.9262678721	5.7370850686	9.8230620138
C3	6.0	10.5990871264	4.7079732467	10.5082409608
C4	6.0	11.5904814440	5.1217280119	11.4783360913
C5	6.0	11.7912974237	6.5118683428	11.7125649425
C6	6.0	11.0259652096	7.4180335284	10.9936390682
C7	6.0	8.8831849772	5.4724282761	8.8171197404
C8	6.0	10.3578956719	3.3385586883	10.3152349155
C9	6.0	12.3348992892	4.1675748598	12.1803334278
C10	6.0	12.8489510763	6.9141298665	12.6924732286
C11	6.0	11.1219937819	8.8832743038	11.1559294258
C12	6.0	11.1010743012	9.4983522039	12.4137859574
C13	6.0	11.1429812020	10.8828990345	12.5298774661
C14	6.0	11.2097871476	11.6810577110	11.3929571340
C15	6.0	11.2272829468	11.0821574978	10.1354783117
C16	6.0	11.1750671382	9.7005648097	10.0188796122

C17	6.0	8.2442605457	6.5733590994	8.2218499365
C18	6.0	8.4094538517	4.2251646545	8.3943708867
N19	7.0	7.6787516973	7.4369258793	7.6947743491
N20	7.0	7.9625454738	3.2310225743	7.9967486620
N21	7.0	10.2060091797	2.1915278888	10.2089963136
N22	7.0	12.9504552345	3.3651522936	12.7600667242
H23	1.0	12.5011272328	6.7830882103	13.7237032809
H24	1.0	13.1461811585	7.9539272493	12.5653778382
H25	1.0	13.7322640898	6.2798353916	12.5748909481
H26	1.0	11.0166559419	8.8903107799	13.3083871451
H27	1.0	11.1118943687	11.3394599728	13.5141615768
H28	1.0	11.2414634016	12.7618460026	11.4846212865
H29	1.0	11.2783207465	11.6964555788	9.2418479515
H30	1.0	11.1702753358	9.2329244475	9.0401463715
LI31	3.0	6.716	9.009	6.797
LI32	3.0	7.226	1.436	7.340

Table S11 Cartesian atomic coordinates (Å) for Li-2 model (two Li+ cations positioned at the cyano groups attached to the pyridine fragment of the TCPy anion (excited state).

Atom	Charge	X	Y	Z
N1	7.0	10.1224641337	7.0184091821	10.0326557809
C2	6.0	9.9262678721	5.7370850686	9.8230620138
C3	6.0	10.5990871264	4.7079732467	10.5082409608
C4	6.0	11.5904814440	5.1217280119	11.4783360913
C5	6.0	11.7912974237	6.5118683428	11.7125649425
C6	6.0	11.0259652096	7.4180335284	10.9936390682
C7	6.0	8.8831849772	5.4724282761	8.8171197404
C8	6.0	10.3578956719	3.3385586883	10.3152349155
C9	6.0	12.3348992892	4.1675748598	12.1803334278
C10	6.0	12.8489510763	6.9141298665	12.6924732286
C11	6.0	11.1219937819	8.8832743038	11.1559294258
C12	6.0	11.1010743012	9.4983522039	12.4137859574
C13	6.0	11.1429812020	10.8828990345	12.5298774661
C14	6.0	11.2097871476	11.6810577110	11.3929571340
C15	6.0	11.2272829468	11.0821574978	10.1354783117
C16	6.0	11.1750671382	9.7005648097	10.0188796122
C17	6.0	8.2442605457	6.5733590994	8.2218499365
C18	6.0	8.4094538517	4.2251646545	8.3943708867
N19	7.0	7.6787516973	7.4369258793	7.6947743491
N20	7.0	7.9625454738	3.2310225743	7.9967486620
N21	7.0	10.2060091797	2.1915278888	10.2089963136
N22	7.0	12.9504552345	3.3651522936	12.7600667242
H23	1.0	12.5011272328	6.7830882103	13.7237032809
H24	1.0	13.1461811585	7.9539272493	12.5653778382
H25	1.0	13.7322640898	6.2798353916	12.5748909481
H26	1.0	11.0166559419	8.8903107799	13.3083871451
H27	1.0	11.1118943687	11.3394599728	13.5141615768
H28	1.0	11.2414634016	12.7618460026	11.4846212865
H29	1.0	11.2783207465	11.6964555788	9.2418479515
H30	1.0	11.1702753358	9.2329244475	9.0401463715
LI31	3.0	9.892	0.180	9.970
LI32	3.0	14.037	1.961	13.785

Table S12 Characteristics of electronic transitions calculated for Li-1 model

STATE#1 ENERGY	2.438720 EV
OSCILLATOR STRENGTH	0.041561
LAMBDADIAGNOSTIC	0.462 (RYDBERG/CHARGE TRANSFER CHARACTER)
SYMMETRYOFSTATE	A

EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
74	76	0.040909	0.013522
75	76	-0.996309	0.040061
71	77	-0.057296	-0.030369
74	77	-0.031650	-0.010844
STATE#2 ENERGY		3.618889 EV	
OSCILLATOR STRENGTH		0.266821	
LAMBDADIAGNOSTIC		0.495 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	
EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
70	76	0.031948	-0.009023
71	76	0.055583	0.018231
72	76	0.120876	-0.002421
73	76	0.068571	0.000478
74	76	-0.982182	0.028191
75	76	-0.037739	0.015394
71	77	-0.035383	-0.010274
75	77	-0.035636	0.002903

Table S13 Characteristics of electronic transitions calculated for Li-2 model

STATE#1 ENERGY		1.726119 EV	
OSCILLATOR STRENGTH		0.020936	
LAMBDADIAGNOSTIC		0.431 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	
EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
71	76	0.032281	0.028886
75	76	0.999271	-0.052430
70	77	-0.035534	-0.026520
STATE#2 ENERGY		3.326174 EV	
OSCILLATOR STRENGTH		0.253117	
LAMBDADIAGNOSTIC		0.481 (RYDBERG/CHARGE TRANSFER CHARACTER)	
SYMMETRYOFSTATE		A	
EXCITATION _DE-EXCITATION			
OCC I	VIR A	AMPLITUDE X(I->A)	AMPLITUDE Y(A->I)
70	76	-0.041349	-0.012429
72	76	-0.135637	0.001932
73	76	-0.076924	-0.000814
74	76	-0.982040	0.031228
70	77	-0.039223	-0.015977

5. Experimental

Materials and apparatus

The progress of reactions and the purity of products were monitored by TLC on Sorbfil plates (spots were visualized under UV light, by treatment with iodine vapor or by heating). The IR spectra were recorded on an FSM-1202 spectrometer with Fourier transform from samples dispersed in mineral oil. The NMR spectra were measured in DMSO‑d6 on a Bruker DRX500 and Bruker AV600 spectrometer using TMS as an internal reference. Elemental analyses were performed using a FlashEA 1112 CHN analyzer. The mass spectra (EI, 70 eV) were obtained on a Finnigan MAT INCOS-50 spectrometer. Melting points were determined on a device OptiMelt MPA-100. Solid-state emission spectra were registered in powders at room temperature on a Cary Eclipse fluorescence spectrophotometer. The fluorescence quantum yield (QY) was determined by the reported procedure and calculated according to the QY = f/(γR0 – R) where, f is the integrated fluorescence of the sample, γ is the calibration factor, R0 is the back-scattered intensity of excitation light from a blank (KBr) and R the back-scattered intensity of a loaded sample. The excitation wavelength (λex 475 nm) was selected from the excitation spectra of the compounds 4. Calibration factor (γ) was found using diffusion reflection in a non-absorbed wavelength (775 nm) from the relative intensities of reflections of the sample and KBr powder. The XRD data of 4a-d were collected by using STOE diffractometer Pilatus100 K detector, focusing mirror collimation Cu Kα (1.54086 Å) radiation, rotation method mode. STOE X-AREA software was used for cells refinement and data reduction. Data collection and image processing was performed with X-Area 1.67 (STOE & Cie GmbH, Darmstadt, Germany, 2013). Intensity data were scaled with LANA (part of X-Area) in order to minimize differences of intensities of symmetry-equivalent reflections (multi-scan method). The structures were solved with SHELXS and refined with SHELXL program.15 The non-hydrogen atoms were refined by using the anisotropic full matrix least-square procedure. Hydrogen atoms were placed in the calculated positions and allowed to ride on their parent atoms. Molecular geometry calculations were performed with the SHELX program.

Synthetic procedures

2-(Dicyanomethylene)-5-methyl-6-phenyl-1,2-dihydropyridine-3,4-dicarbo-nitrile (**TCPy**) 1 g (3.53 mmol) was dissolved in 20 ml of organic solvent, then 3.59 mmol of the corresponding metal acetate was added. The reaction mixture was stirred at 50 ºC for 3 min. Further precipitate crystals were filtered off, washed with organic solvent (20 ml) twice. The resulting product was dried in a vacuum desiccator.

Characterization

Lithium 3,4-dicyano-2-(dicyanomethylene)-5-methyl-6-phenyl-2H-pyridin-1-ide (**2a**). Yellow solid. Yield: 95%. mp 178-179 °C (dec.). IR (KBr): 2200, 2183 (CN), 1664, 1534 cm^{-1}. ^{1}H NMR (500.13 MHz, DMSO‑d_6): δ= 2.26 (s, 3H, CH_3), 7.46–7.54 (m, 5H, Ar). ^{13}C NMR (125.76 MHz, DMSO‑d_6): δ=18.04 (CH_3), 41.05 ($C(CN)_2$), 92.41 (β-Pyr), 115.39 (CN), 115.74 (CN), 121.70 (2CN), 122.25, 126.22, 128.50, 129.13, 129.44, 139.03, 159.03, 161.90, 176.52. Anal. calcd for $C_{17}H_8LiN_5$*$2H_2O$: C, 62.78; H, 3.72; N, 21.53. Found: C, 62.70; H, 3.78; N, 21.46.

Sodium 3,4-dicyano-2-(dicyanomethylene)-5-methyl-6-phenyl-2H-pyridin-1-ide (**2b**). Orange solid. Yield: 96%. mp 261-262 °C (dec.). IR (KBr): 2200, 2183 (CN), 1664, 1534 cm^{-1}. ^{1}H NMR (500.13 MHz, DMSO‑d_6): δ=2.26 (s, 3H, CH_3), 7.46–7.54 (m, 5H, Ar). ^{13}C NMR (125.76 MHz, DMSO‑d_6): δ=18.05 (CH_3), 92.41 (β-Pyr), 115.39 (CN), 115.74 (CN), 121.69 (2CN), 122.22,

128.50, 129.13, 129.43, 139.05, 159.05, 161.90. Anal. calcd for $C_{17}H_8NaN_5*H_2O$: C, 63.16; H, 3.12; N, 21.66. Found: C, 63.03; H, 3.18; N, 21.59.

Potassium 3,4-dicyano-2-(dicyanomethylene)-5-methyl-6-phenyl-2H-pyridin-1-ide (**2c**). Orange solid. Yield: 95%. mp 265-266 °C (dec.). IR (KBr): 2200, 2183 (CN), 1664, 1534 cm^{-1}. ^1H NMR (500.13 MHz, DMSO-d_6): δ= 2.26 (s, 3H, CH_3), 7.46–7.54 (m, 5H, Ar). ^{13}C NMR (125.76 MHz, DMSO-d_6): δ=18.05 (CH_3), 41.08 ($C(CN)_2$), 92.41 (β-Pyr), 115.38 (CN), 115.76 (CN), 121.70 (2CN), 122.23, 126.22, 128.50, 128.65, 128.96, 129.13, 129.43, 139.03, 159.05, 161.90. Anal. calcd for $C_{17}H_8KN_5$: C, 63.53; H, 2.51; N, 21.79. Found: C, 63.40; H, 2.56; N, 21.71

Rubidium 3,4-dicyano-2-(dicyanomethylene)-5-methyl-6-phenyl-2H-pyridin-1-ide (**2d**). Orange solid. Yield: 93%. mp 212–213 °C (dec.). IR (KBr): 2200, 2183 (CN), 1664, 1534 cm^{-1}. ^1H NMR (500.13 MHz, DMSO-d_6): δ= 2.26 (s, 3H, CH_3), 7.46–7.54 (m, 5H, Ar). ^{13}C NMR (125.76 MHz, DMSO-d_6): δ=18.05 (CH_3), 41.09 ($C(CN)_2$), 92.41 (β-Pyr), 115.39 (CN), 115.77 (CN), 121.70, (2CN), 122.22, 126.22, 128.50, 129.13, 129.44, 139.04, 159.05, 161.90. Anal. calcd for $C_{17}H_8N_5Rb$: C, 55.52; H, 2.19; N, 19.04. Found: C, 55.38; H, 2.23; N, 18.97.

Cesium 3,4-dicyano-2-(dicyanomethylene)-5-methyl-6-phenyl-2H-pyridin-1-ide (**2e**). Orange solid. Yield: 93%. mp 303–304 °C (dec.). IR (KBr): 2200, 2183 (CN), 1664, 1534 cm^{-1}. ^1H NMR (500.13 MHz, DMSO-d_6): δ= 2.25 (s, 3H, CH_3), 7.46–7.54 (m, 5H, Ar). ^{13}C NMR (125.76 MHz, DMSO-d_6): δ=17.72 (CH_3), 40.75 ($C(CN)_2$), 92.07 (β-Pyr), 115.07 (CN), 115.43 (CN), 121.36 (2CN), 121.89, 125.89, 128.17, 128.81, 129.11, 138.71, 158.71, 161.56. Anal. calcd for $C_{17}H_8CsN_5*CH_3OH$: C, 48.34; H, 2.70; N, 15.66. Found: C, 48.21; H, 2.73; N, 15.60.

5. NMR spectra

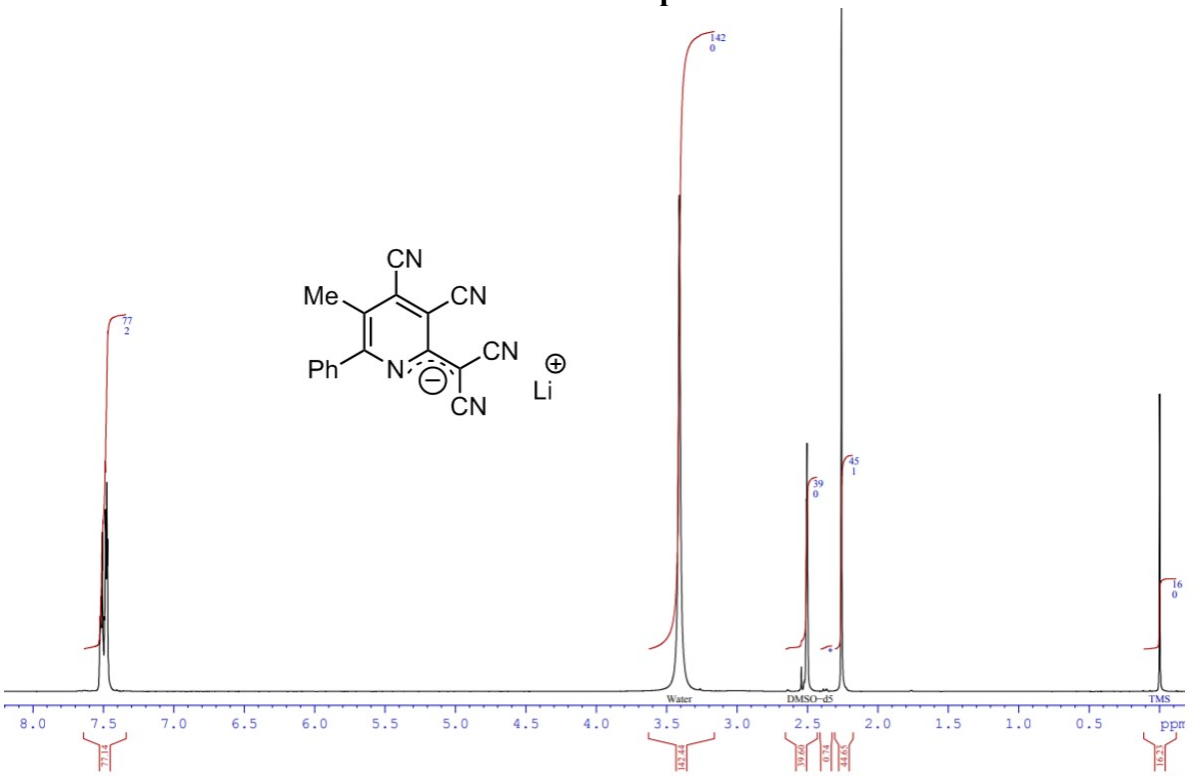

Figure S17 ^{1}H NMR-spectrum of **2a** (500.13 MHz, DMSO−d_6).

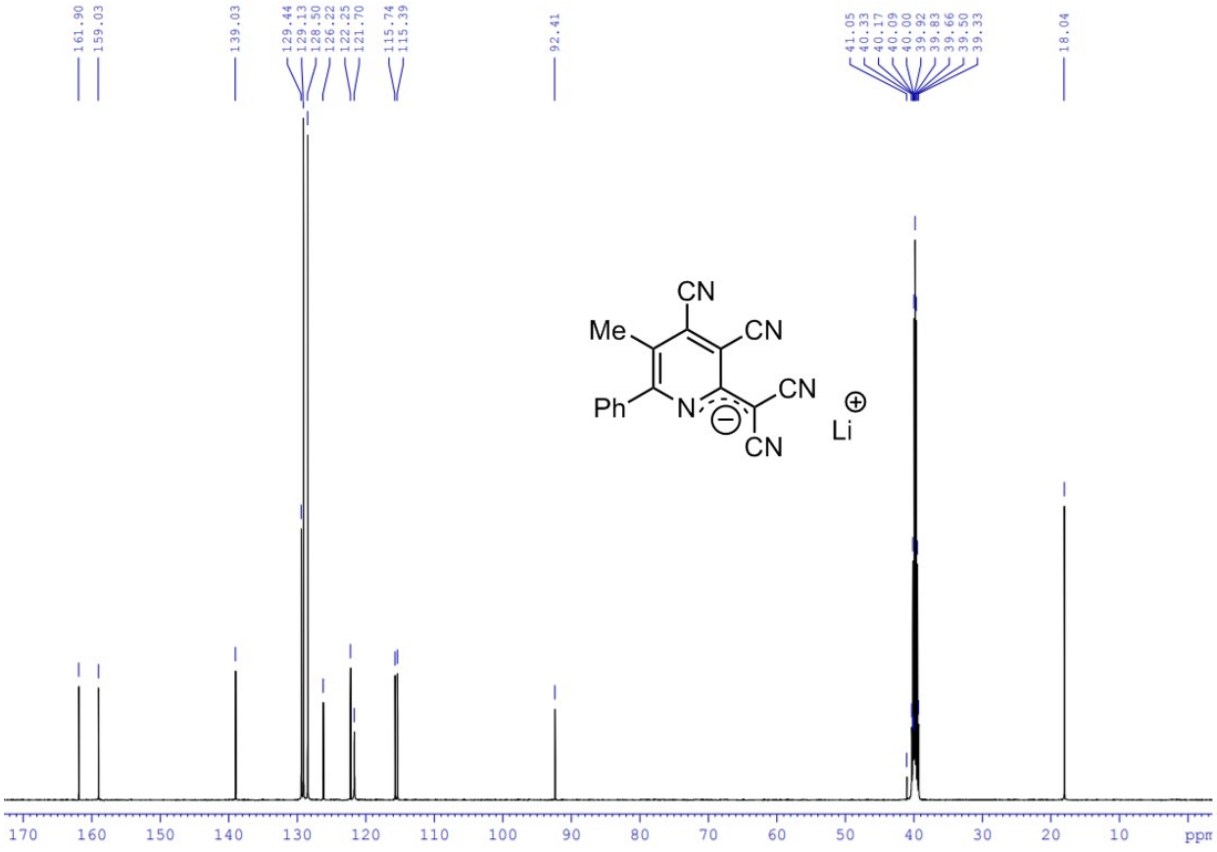

Figure S18 ^{13}C NMR-spectrum of **2a** (500.13 MHz, DMSO−d_6).

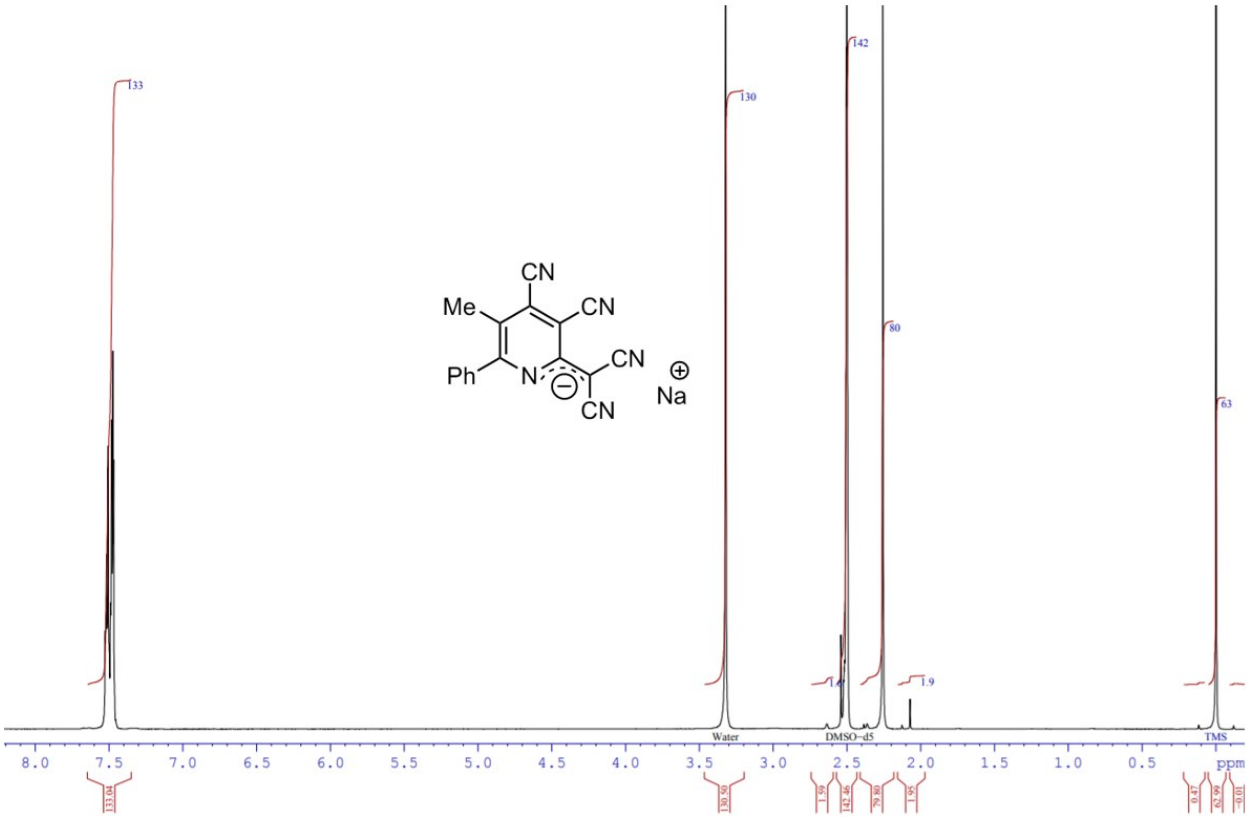

Figure S19 ^{1}H NMR-spectrum of **2b** (500.13 MHz, DMSO−d_6).

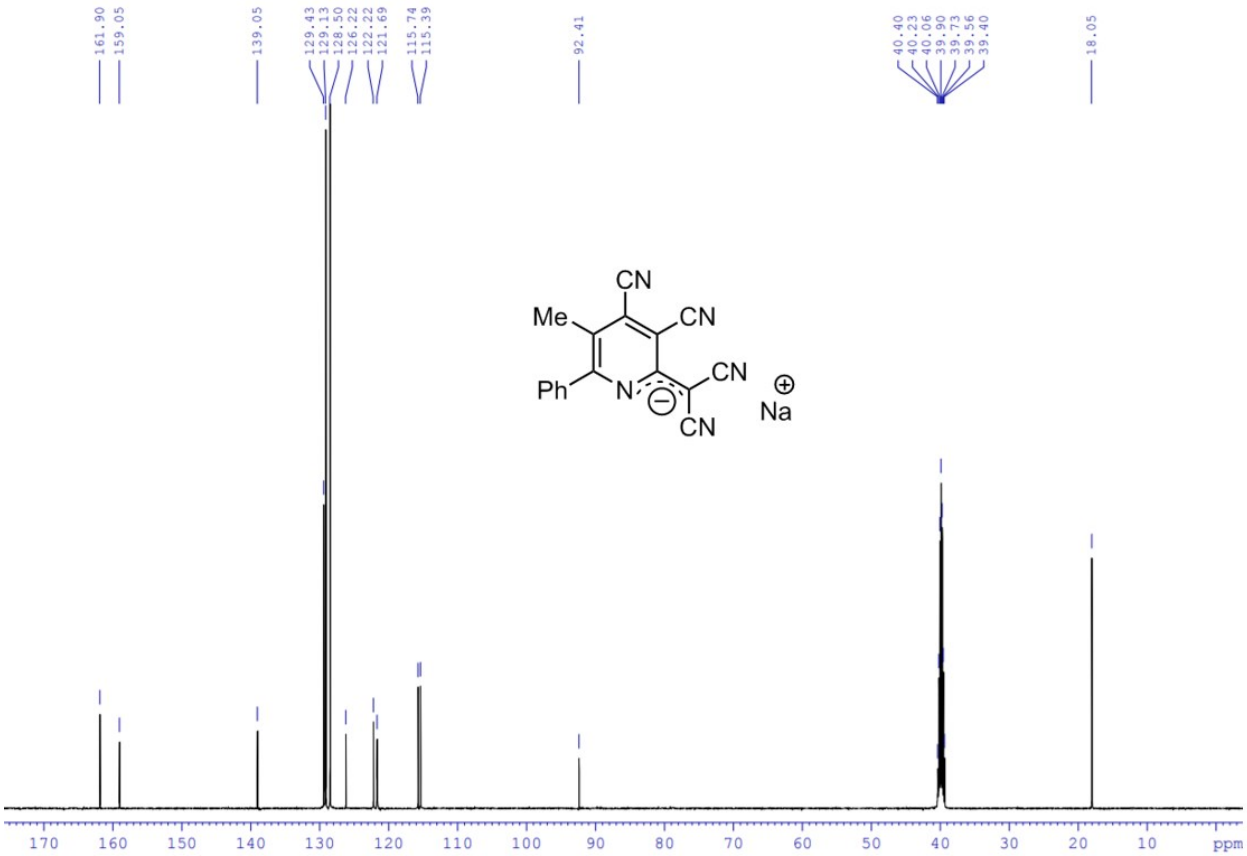

Figure S20 ^{13}C NMR-spectrum of **2b** (500.13 MHz, DMSO−d_6).

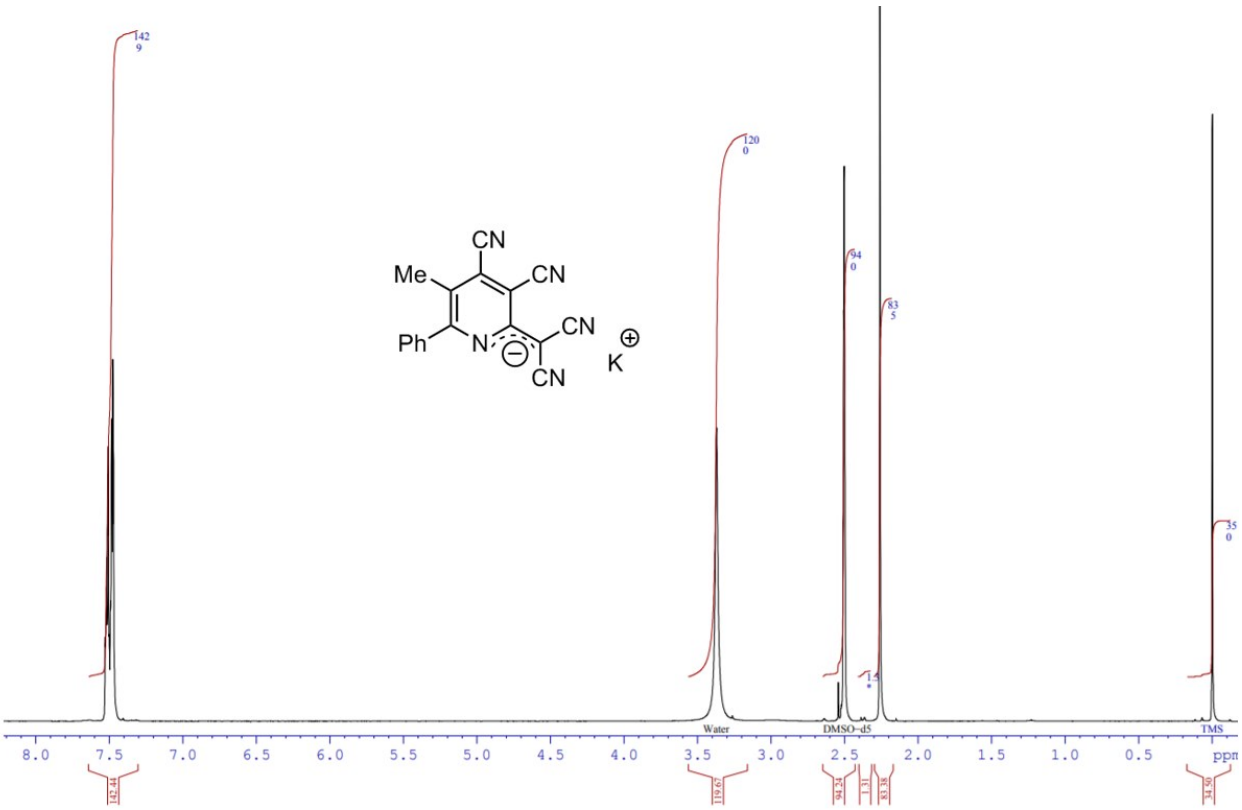

Figure S21 ^{1}H NMR-spectrum of **2c** (500.13 MHz, DMSO−d_6).

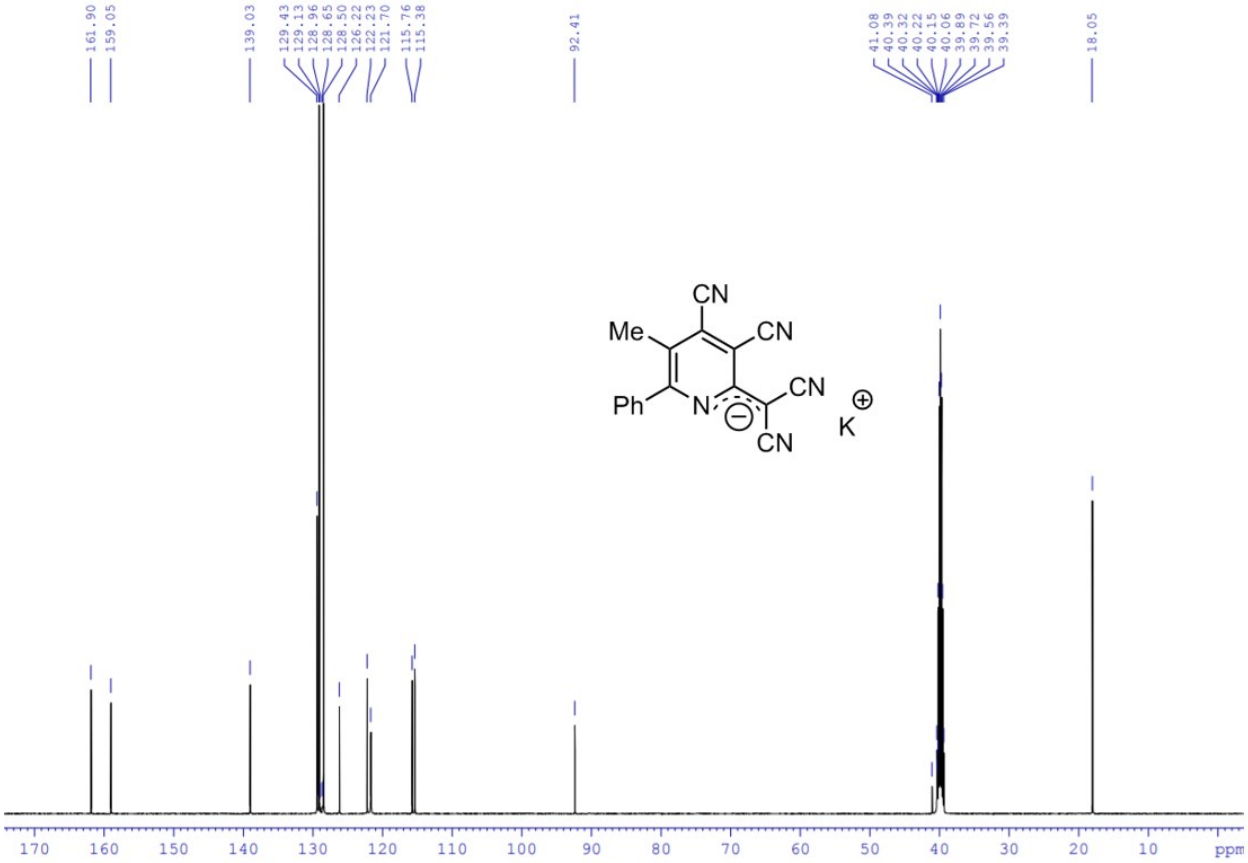

Figure S22 ^{13}C NMR-spectrum of **2c** (500.13 MHz, DMSO−d_6).

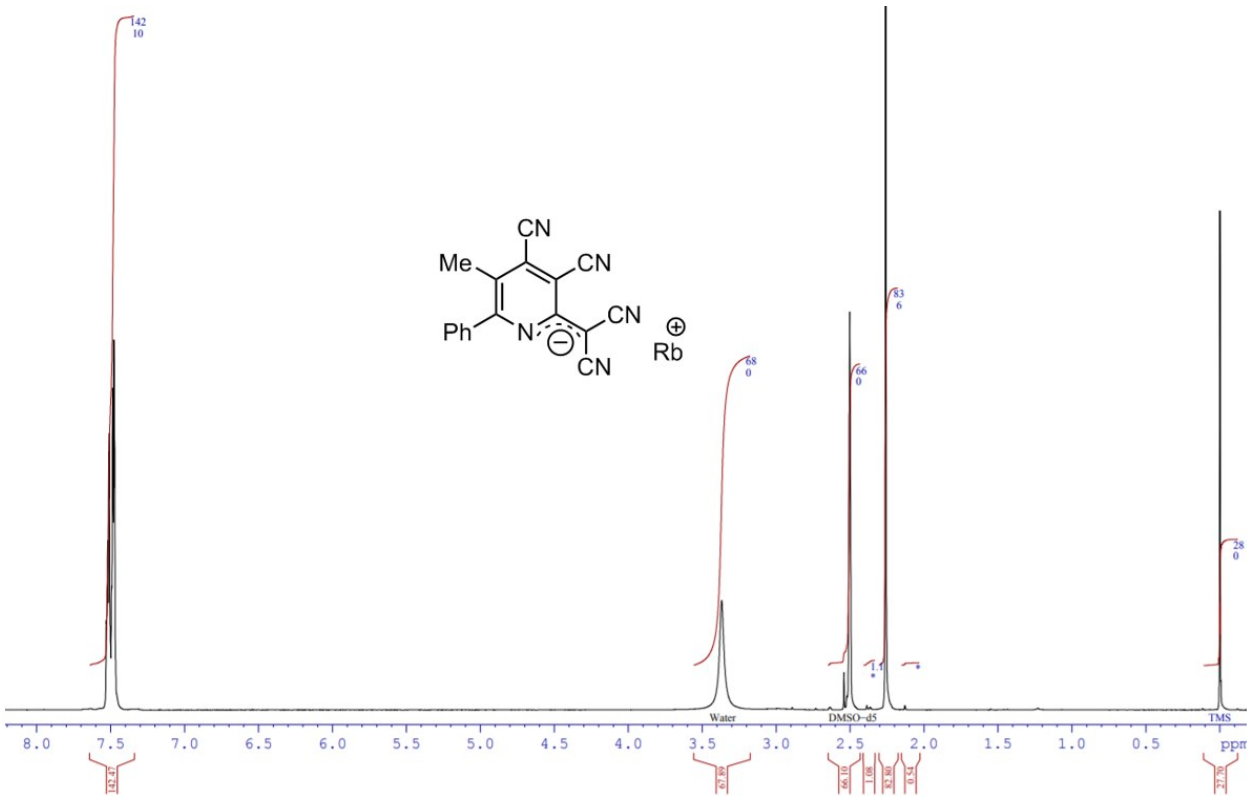

Figure S23 ^{1}H NMR-spectrum of **2d** (500.13 MHz, DMSO−d_6).

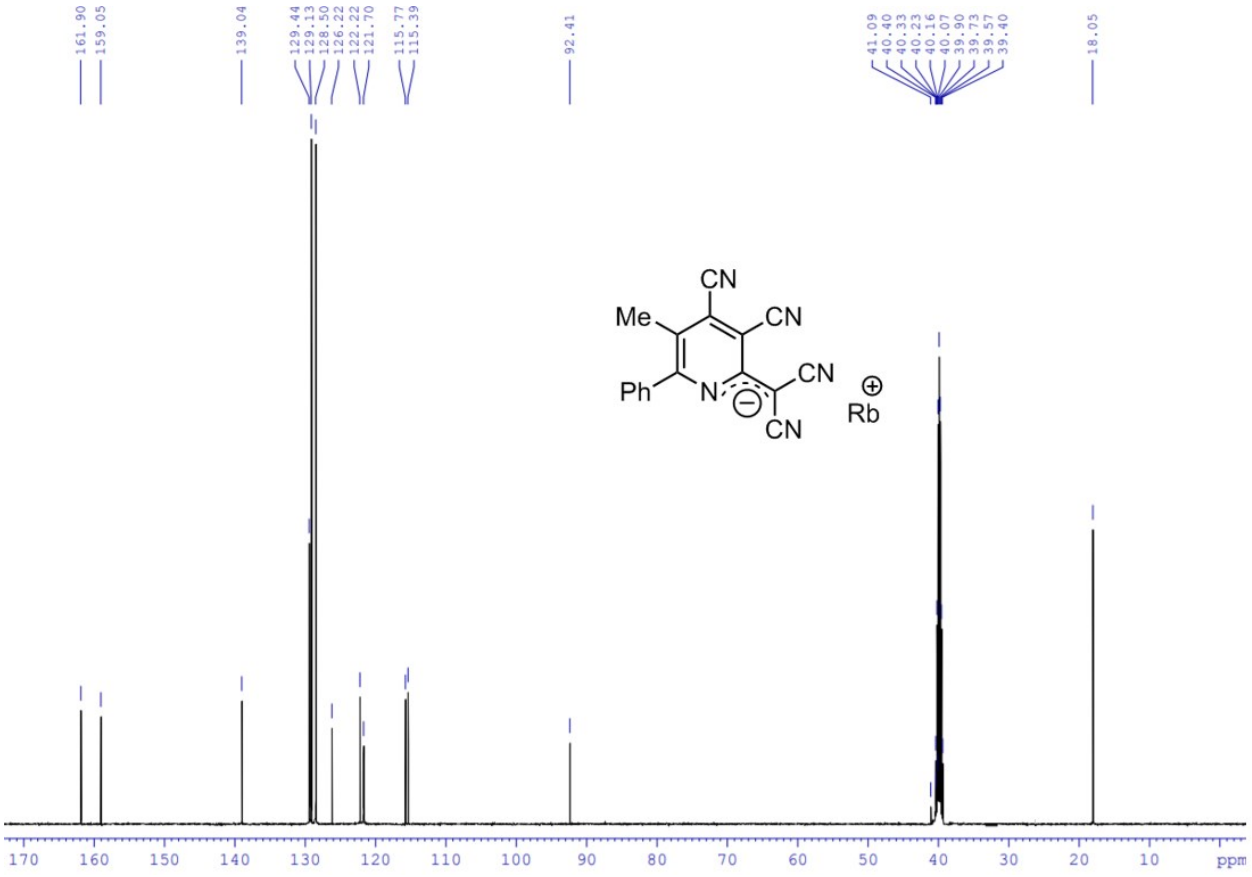

Figure S24 ^{13}C NMR-spectrum of **2d** (500.13 MHz, DMSO−d_6).

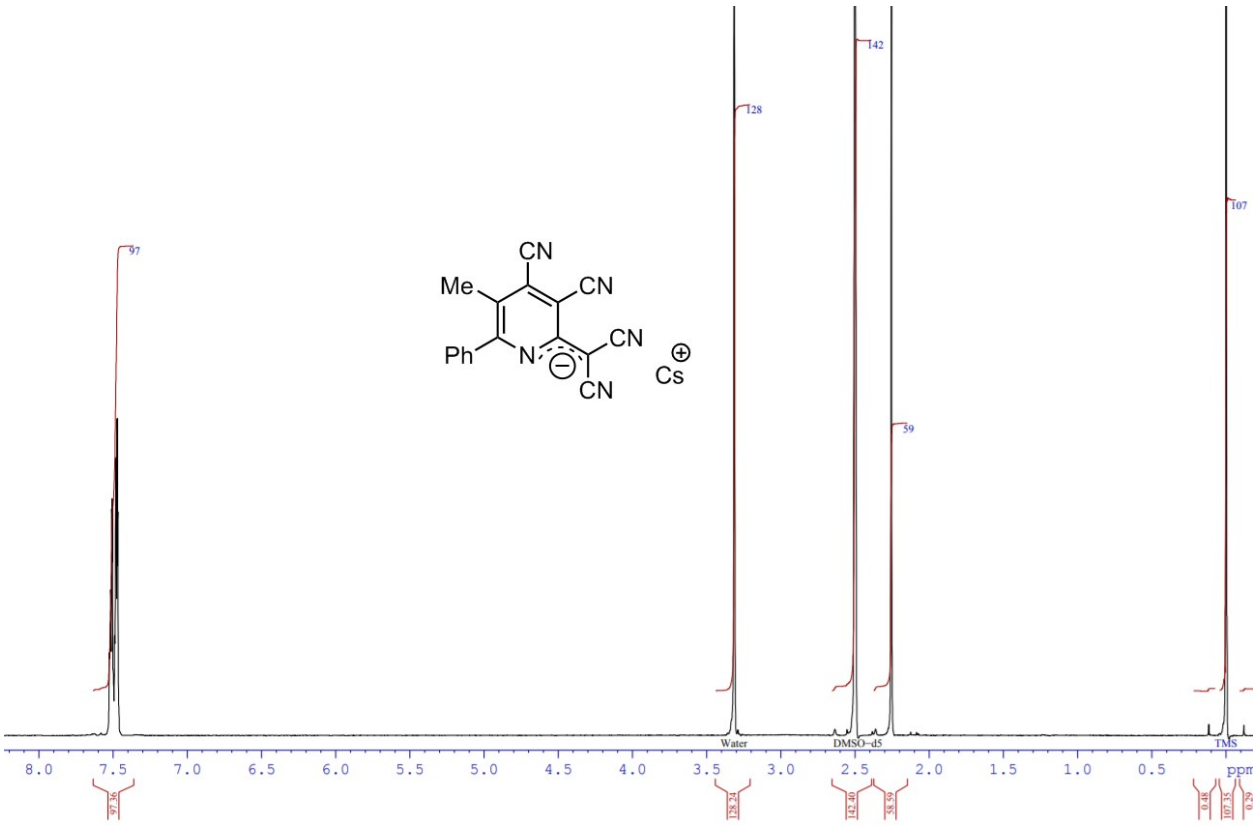

Figure S25 ^{1}H NMR-spectrum of **2e** (500.13 MHz, DMSO−d_6).

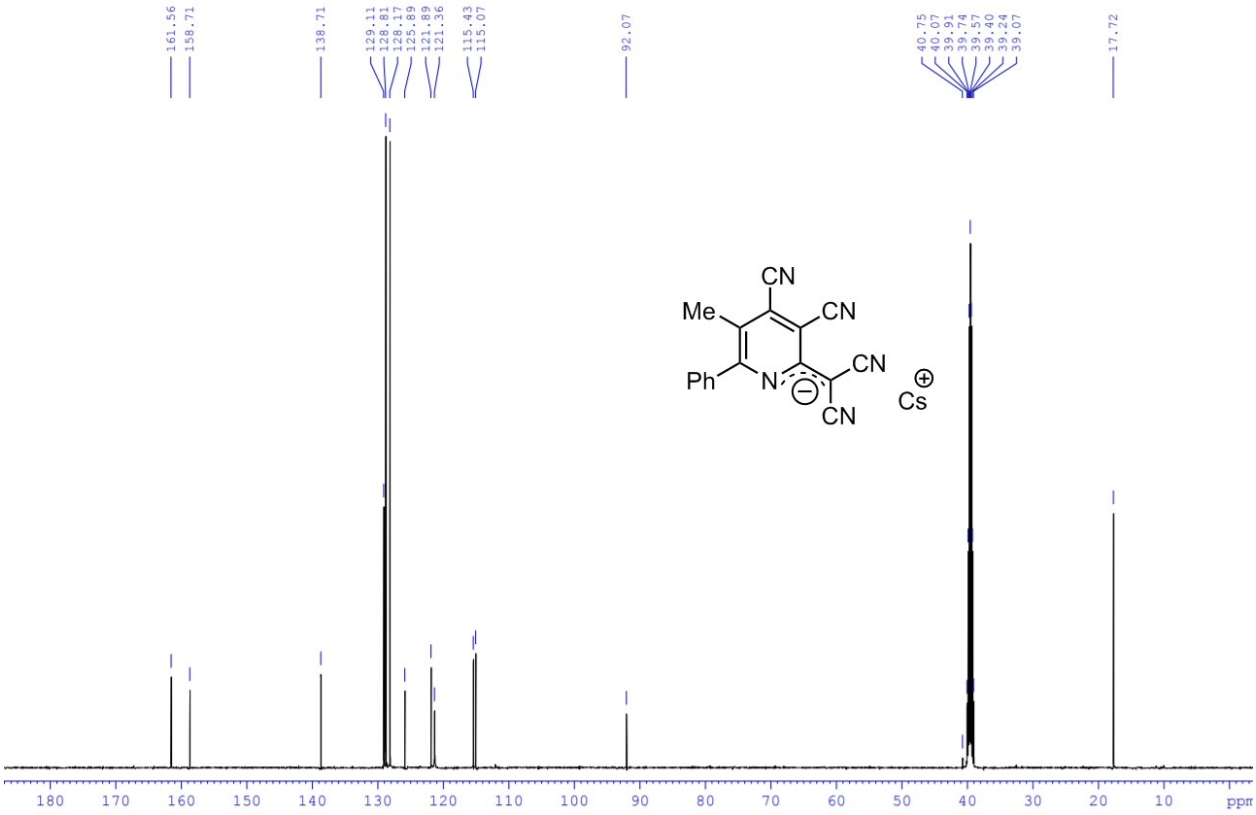

Figure S26 ^{13}C NMR-spectrum of **2e** (500.13 MHz, DMSO−d_6).