Supporting Information

The Reduction of Pyridine by $K_{12}Si_{17}$ to the 4,4'- Bipyridine Radical Anion $[C_{10}H_8N_2]^{-\bullet}$: Crystal Structure and Spectroscopic Characterization

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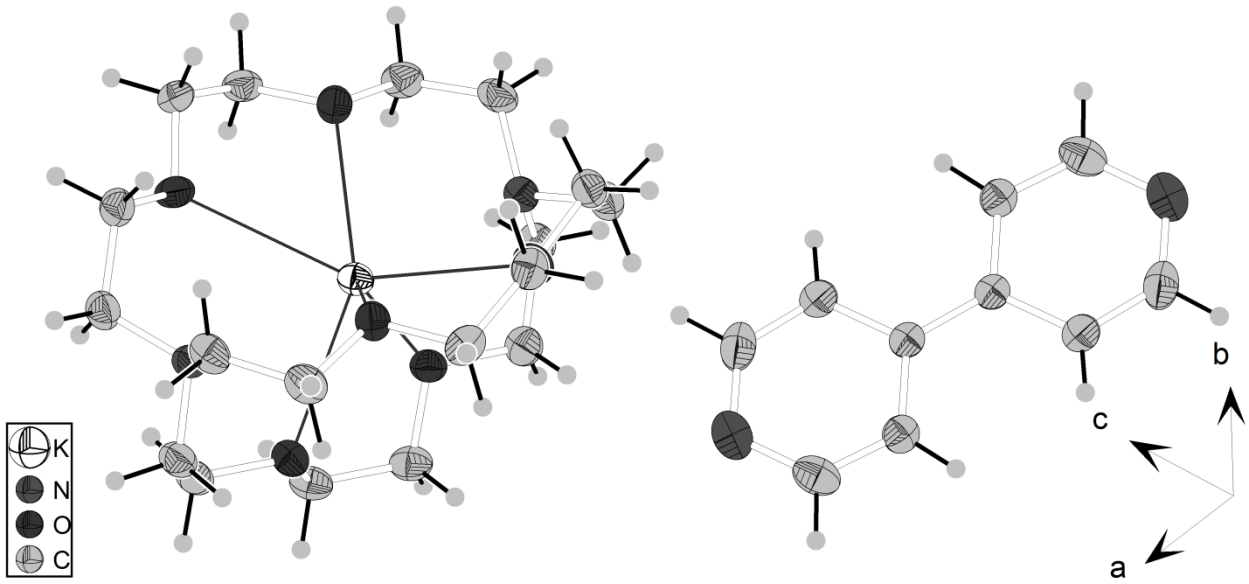

Figure S1: Asymmetric unit completed by symmetry operations of the crystal structure of **1**. Anisotropic displacement ellipsoids of all atoms are drawn at the 50 % probability level at 150 K.

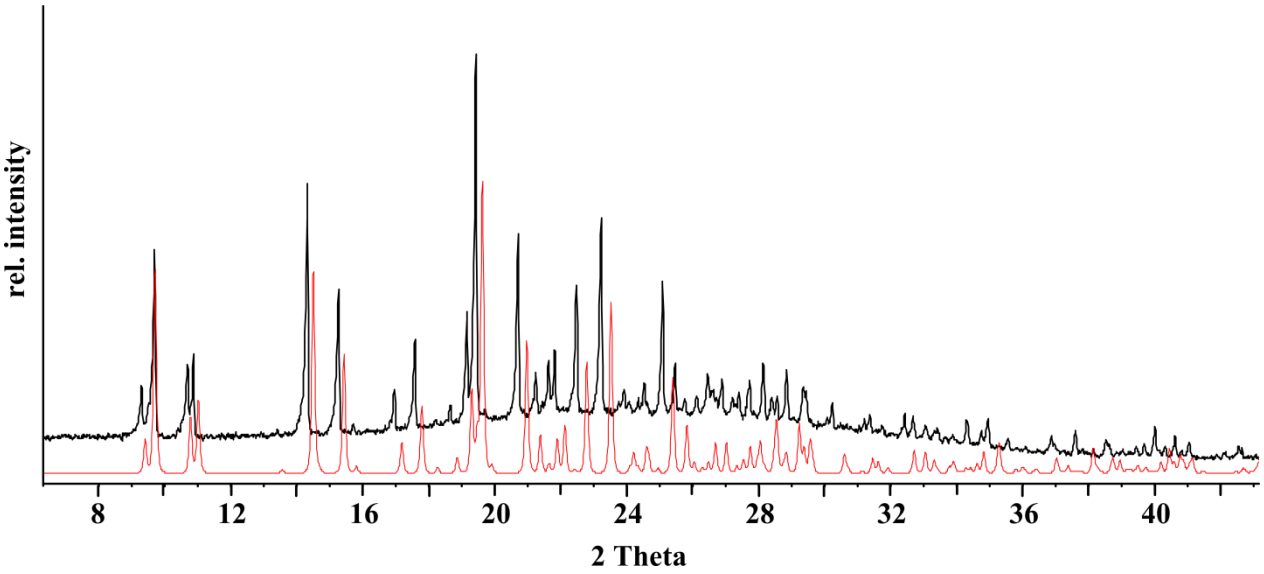

Figure S2: Powder X-ray diffraction pattern of compound **1** at 298(2) K (black) and calculated diffraction pattern based on the data set of the single-crystal diffraction at 150(2) K (red). P-XRD data were collected at on a Stoe diffractometer in Debye-Scherrer geometry using CuKα_1 radiaton (1.54056 Å) equipped with a position-sensitive detector (Mythen).

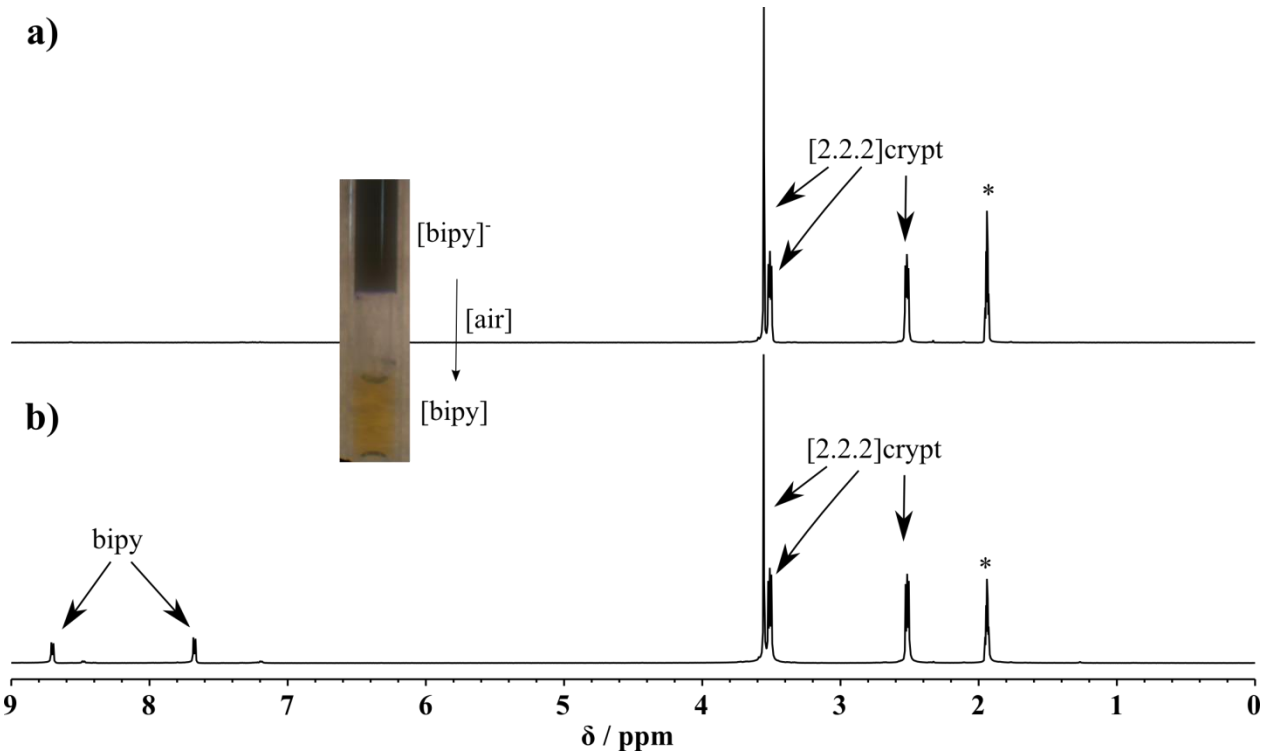

Figure S3: ^{1}H NMR spectra of **a)** compound **1** in CD_3CN (*) freshly prepared (deep-purple solution) and **b)** after exposure to air (almost colorless solution).

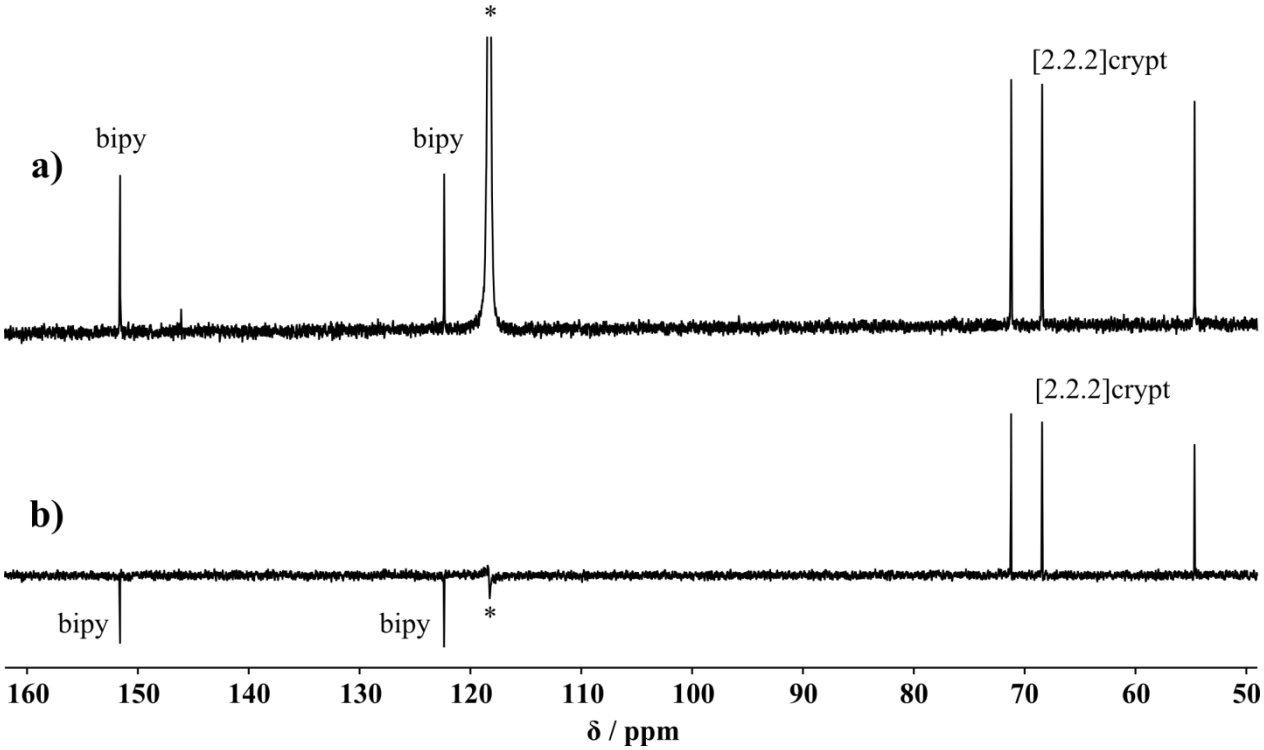

Figure S4: a) ^{13}C NMR and **b)** ^{13}C DEPT NMR spectra (CH, CH_3 negative, CH_2 positive) of compound **1** in CD_3CN (*) after exposure to air (colorless solution).

Table S1: Chemical shifts δ (ppm) and assignments for the ^{1}H und ^{13}C NMR spectra of compound **1** after exposure to air (**1'**) in CD_3CN at 298(2) K.

^{1}H NMR, **1'**		^{13}C NMR, **1'**	
δ	Assignment	δ	Assignment
8.70 (4.5, 1.6 Hz)	bipy-$C_{\alpha}H$	151.60	bipy-C_{α}
7.67 (4.5, 1.7 Hz)	bipy-$C_{\beta}H$	146.10	bipy-C_{γ}
		122.37	bipy-C_{β}
3.56	[2.2.2]crypt	71.21	[2.2.2]crypt
3.51	[2.2.2]crypt	68.42	[2.2.2]crypt
2.52	[2.2.2]crypt	54.67	[2.2.2]crypt

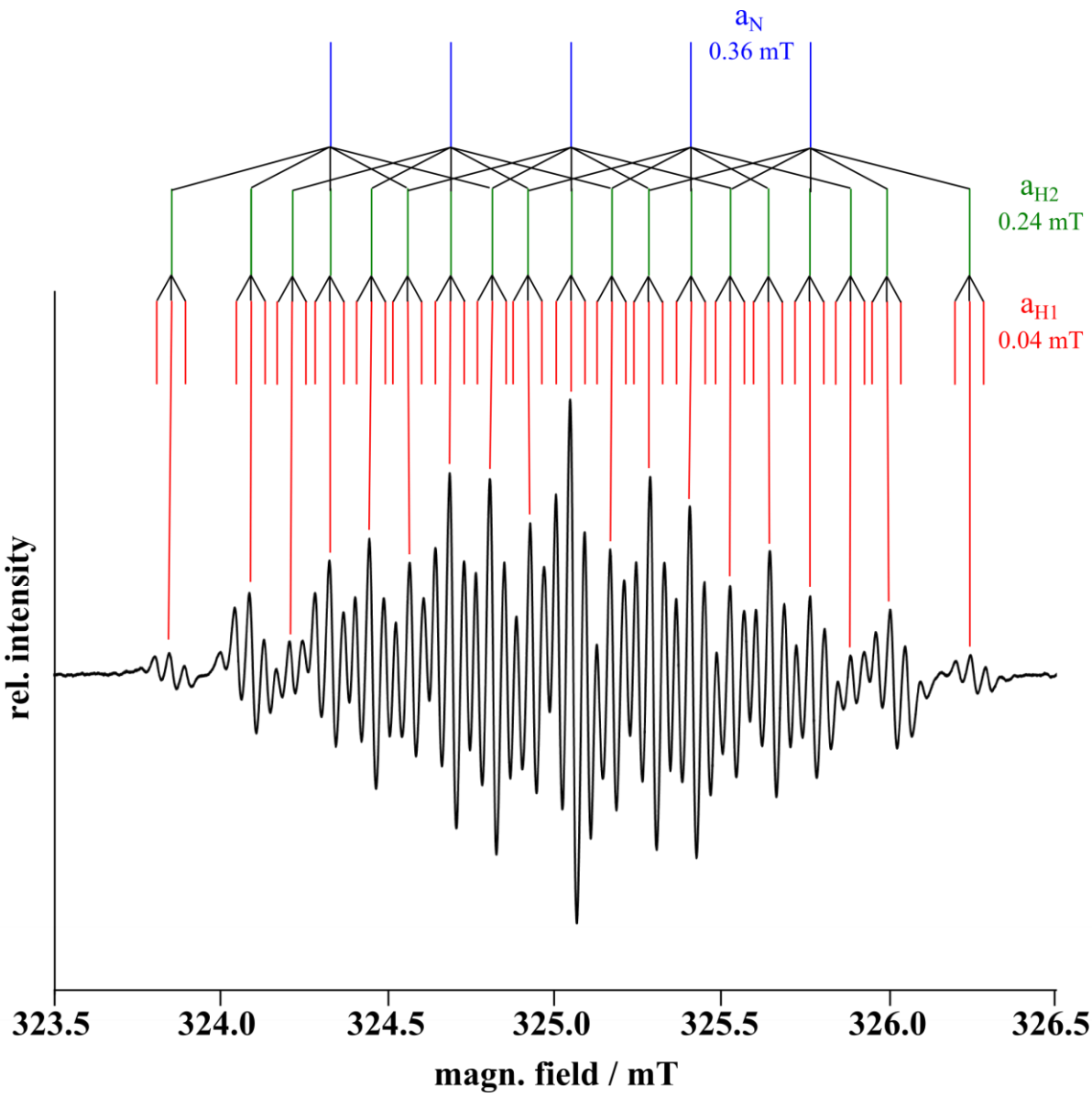

Figure S5: EPR spectrum of compound **1** in ethylenediamine measured with an Mn standard (*).

Two N atoms (spin, I = 1) in the radical anion of **1** generate five signals with a hyperfine coupling constant of a_N = 0.36 mT (blue). Each of these signal splits to a quintet with a_{H2} = 0.24 mT (green) due to four H atoms (spin, I = ½). Additional splitting of each signal occurs with a_{H1} = 0.04 mT (red). Compound **1**: *g* = 1.95069. For comparison the *g* value for the Na(4,4'-bipy)·(en) is reported with *g* = 2.00429 [1].

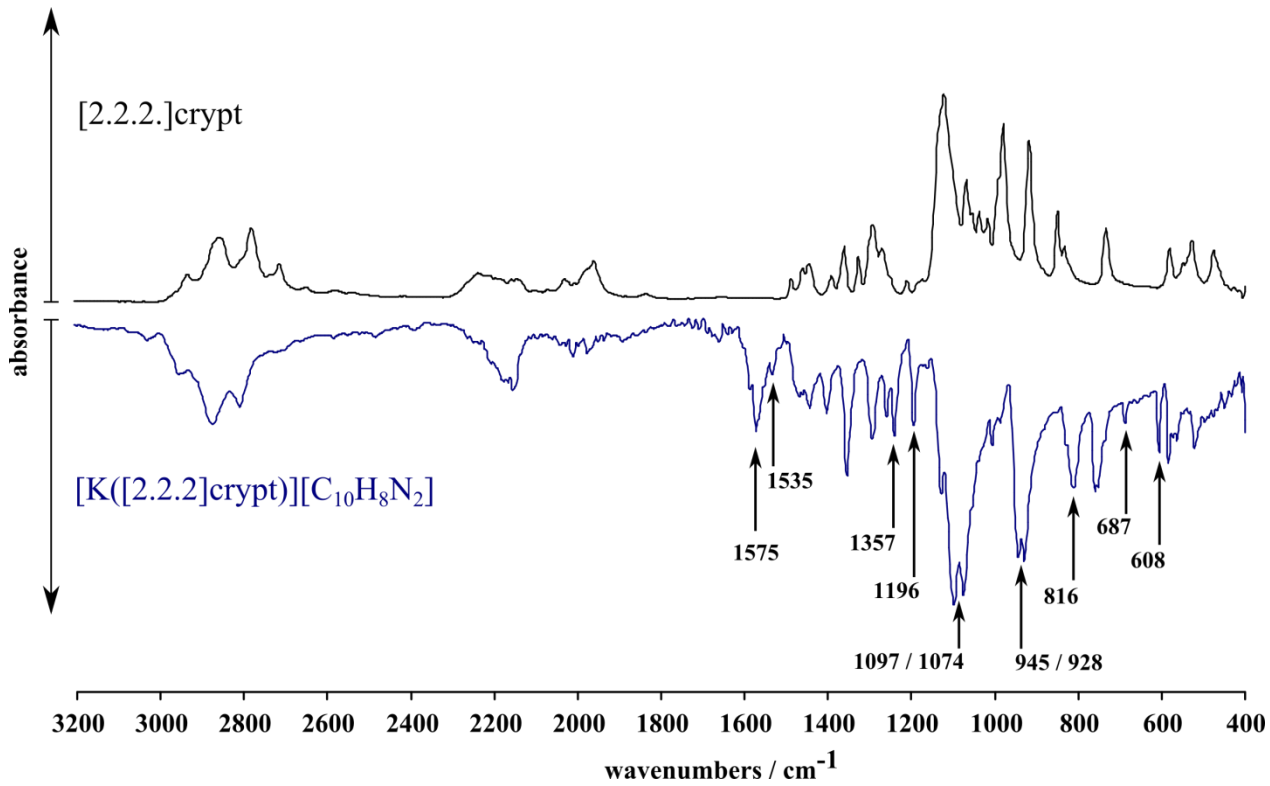

Figure S6: IR spectra of compound **1** in a KBr sandwich disc (transmission mode) and of pure [2.2.2]crypt (total reflection mode, ATR) for comparison. Values in brackets are the corresponding transmittance (given in %) of each band. 3074 (75), 3031 (71), 2975 (63), 2960 (63), 2881 (51), 2811 (57), 1575 (35), 1471 (70), 1458 (73), 1440 (76), 1400 (79), 1382 (84), 1357 (60), 1344 (73), 1294 (65), 1257 (74), 1242 (57), 1197 (53), 1162 (79), 1128 (54), 1097 (31), 1078 (47), 1056 (72), 1008 (78), 945 (36), 929 (57), 829 (57), 817 (80), 761 (64), 688 (82), 586 (75).

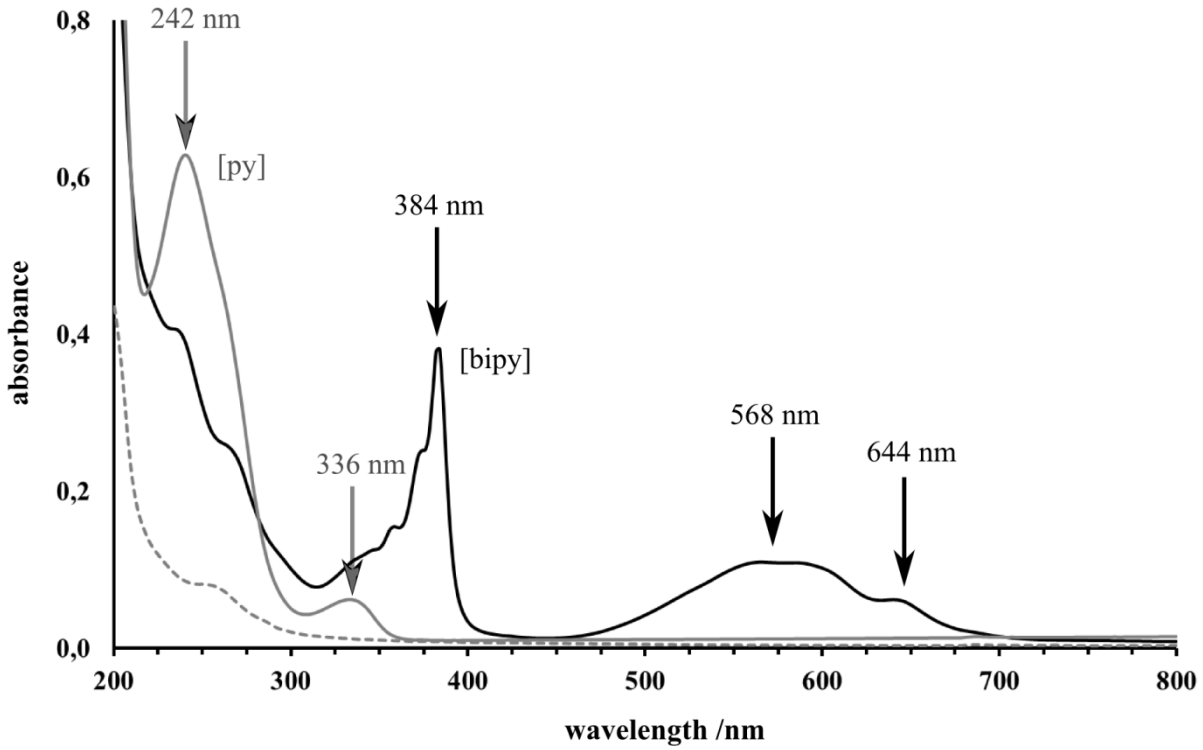

Figure S7: Electronic spectra of compound **1** dissolved in anhydrous acetonitrile (black), after exposure to air (grey, solid) and of pure acetonitrile for comparison (grey, dashed).

The (black) spectrum of a deep-purple solution of compound **1** in acetonitrile shows three dominant bands with maxima of absorbance (λ_{max}) at 384 nm, 568 nm and 644 nm; the first two bands correspond to the bipyridinyl radical anions dissolved in pyridine with maxima at 381 nm and 570 nm according to literature [2]. When this solution is exposed to air a color change to light yellow is observed as described above. The corresponding spectrum (grey) exhibits two bands with their maxima at 242 nm and 336 nm. In the literature these bands are assigned to monomeric pyridine radicals with absorbance at 244 nm and 330 nm [2].

Table S2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for compounf **1**.

	x	***y***	***z***	U_{iso}*/U_{eq}
K	0.7500	0.97844 (5)	0.2500	0.02511 (14)
N1	0.48461 (10)	0.98090 (14)	0.21060 (7)	0.0257 (3)
O1	0.65849 (9)	1.09481 (12)	0.09418 (6)	0.0312 (3)
O2	0.62197 (8)	0.67536 (11)	0.24382 (6)	0.0280 (3)
O3	0.59820 (8)	1.12899 (12)	0.36039 (6)	0.0297 (3)
C1	0.45873 (14)	1.0316 (2)	0.12568 (10)	0.0309 (4)
H1A	0.4680 (11)	0.9332 (17)	0.0922 (7)	0.024 (4)*
H1B	0.3744 (12)	1.0747 (16)	0.1187 (8)	0.030 (4)*
C2	0.54193 (14)	1.1631 (2)	0.09577 (11)	0.0306 (4)
H2A	0.5178 (12)	1.1963 (17)	0.0392 (9)	0.037 (4)*
H2B	0.5393 (12)	1.2614 (17)	0.1306 (9)	0.036 (5)*
C3	0.73795 (15)	1.1975 (2)	0.05084 (11)	0.0305 (4)
H3A	0.7090 (11)	1.2055 (15)	-0.0071 (9)	0.028 (4)*
H3B	0.7389 (12)	1.3106 (18)	0.0725 (8)	0.037 (4)*
C4	0.43515 (15)	0.8141 (2)	0.22358 (11)	0.0309 (4)
H4A	0.4224 (11)	0.7995 (15)	0.2822 (8)	0.026 (4)*
H4B	0.3575 (12)	0.8041 (16)	0.1952 (8)	0.029 (4)*
C5	0.51384 (14)	0.6764 (2)	0.19515 (11)	0.0314 (4)
H5A	0.4757 (12)	0.5671 (18)	0.2025 (7)	0.030 (4)*
H5B	0.5317 (12)	0.6896 (15)	0.1344 (9)	0.034 (4)*
C6	0.69389 (14)	0.5363 (2)	0.22449 (10)	0.0313 (4)
H6A	0.6507 (11)	0.4357 (17)	0.2365 (7)	0.030 (4)*
H6B	0.7101 (11)	0.5365 (15)	0.1638 (8)	0.032 (4)*
C7	0.43272 (15)	1.1019 (2)	0.26656 (10)	0.0322 (4)
H7A	0.4509 (11)	1.2153 (17)	0.2483 (7)	0.023 (4)*
H7B	0.3457 (12)	1.0934 (15)	0.2640 (7)	0.024 (4)*
C8	0.47540 (14)	1.0853 (2)	0.35320 (10)	0.0329 (4)
H8A	0.4288 (12)	1.1560 (17)	0.3868 (8)	0.037 (4)*
H8B	0.4656 (12)	0.9673 (18)	0.3756 (8)	0.035 (4)*
C9	0.64071 (15)	1.1227 (2)	0.44322 (10)	0.0305 (4)
H9A	0.5869 (11)	1.1857 (15)	0.4768 (7)	0.022 (4)*
H9B	0.6408 (12)	1.0017 (17)	0.4619 (8)	0.034 (4)*
C10	0.05623 (12)	0.47615 (17)	0.01742 (8)	0.0243 (3)
C11	0.09478 (15)	0.5209 (2)	0.09748 (10)	0.0333 (4)
H11	0.0444 (12)	0.5775 (16)	0.1311 (8)	0.028 (4)*

	x	*y*	*z*	U_{iso}*/U_{eq}
C12	0.20450 (16)	0.4759 (2)	0.12779 (11)	0.0417 (4)
H12	0.2246 (12)	0.5063 (17)	0.1837 (9)	0.044 (5)*
N2	0.28644 (12)	0.38616 (17)	0.08871 (9)	0.0450 (4)
C13	0.24874 (16)	0.3399 (2)	0.01304 (12)	0.0384 (4)
H13	0.3031 (13)	0.2705 (18)	-0.0169 (8)	0.040 (5)*
C14	0.14174 (14)	0.37905 (18)	-0.02367 (10)	0.0289 (4)
H14	0.1242 (11)	0.3400 (14)	-0.0772 (8)	0.016 (4)*

Table S3: Atomic displacement parameters (Å^2).

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
K	0.0224 (3)	0.0248 (3)	0.0282 (3)	0.000	0.0035 (2)	0.000
N1	0.0225 (7)	0.0258 (7)	0.0288 (7)	-0.0017 (6)	0.0015 (6)	0.0012 (6)
O1	0.0285 (6)	0.0292 (6)	0.0360 (6)	-0.0016 (5)	0.0041 (5)	0.0098 (5)
O2	0.0257 (6)	0.0242 (6)	0.0340 (6)	0.0011 (5)	0.0007 (5)	-0.0035 (5)
O3	0.0237 (6)	0.0397 (7)	0.0257 (6)	0.0001 (5)	0.0030 (5)	-0.0020 (5)
C1	0.0260 (10)	0.0313 (10)	0.0352 (10)	0.0002 (9)	-0.0045 (8)	0.0002 (9)
C2	0.0299 (10)	0.0297 (10)	0.0320 (11)	0.0018 (8)	-0.0038 (8)	0.0018 (9)
C3	0.0368 (11)	0.0274 (10)	0.0269 (10)	-0.0053 (9)	-0.0009 (8)	0.0062 (9)
C4	0.0237 (10)	0.0319 (10)	0.0371 (11)	-0.0041 (8)	0.0007 (9)	0.0008 (9)
C5	0.0282 (10)	0.0287 (11)	0.0371 (11)	-0.0054 (8)	-0.0008 (9)	-0.0012 (9)
C6	0.0325 (9)	0.0219 (9)	0.0398 (11)	-0.0023 (8)	0.0055 (8)	-0.0016 (8)
C7	0.0195 (9)	0.0325 (10)	0.0446 (11)	0.0039 (9)	0.0029 (8)	-0.0036 (9)
C8	0.0256 (10)	0.0374 (11)	0.0362 (11)	-0.0002 (9)	0.0092 (8)	-0.0052 (9)
C9	0.0360 (11)	0.0305 (11)	0.0253 (10)	0.0077 (8)	0.0076 (8)	-0.0012 (8)
C10	0.0286 (8)	0.0198 (8)	0.0245 (9)	-0.0042 (8)	0.0019 (7)	0.0025 (7)
C11	0.0372 (10)	0.0324 (10)	0.0302 (10)	0.0020 (9)	-0.0010 (9)	-0.0033 (8)
C12	0.0462 (12)	0.0458 (11)	0.0323 (11)	-0.0040 (10)	-0.0102 (9)	0.0007 (9)
N2	0.0379 (9)	0.0496 (9)	0.0470 (10)	0.0023 (8)	-0.0056 (8)	0.0066 (8)
C13	0.0338 (11)	0.0359 (11)	0.0462 (12)	0.0049 (9)	0.0100 (10)	0.0067 (9)
C14	0.0327 (10)	0.0290 (10)	0.0250 (10)	-0.0013 (8)	0.0026 (8)	0.0031 (8)

Table S4: Geometric parameters (Å, deg) for [K([2.2.2]crypt)][$C_{10}H_8N_2$] (**1**).

K—O3	2.8020 (9)	C4—H4A	0.985 (13)
K—O3^{i}	2.8020 (9)	C4—H4B	0.978 (14)
K—O2	2.8274 (10)	C5—H5A	0.986 (14)
K—O2^{i}	2.8274 (10)	C5—H5B	1.030 (14)
K—O1	2.8818 (9)	C6—C6^{i}	1.489 (3)
K—O1^{i}	2.8818 (9)	C6—H6A	0.966 (13)
K—N1^{i}	3.0261 (11)	C6—H6B	1.019 (13)
K—N1	3.0261 (11)	C7—C8	1.492 (2)
N1—C4	1.4684 (18)	C7—H7A	0.983 (13)
N1—C7	1.4708 (18)	C7—H7B	0.978 (12)
N1—C1	1.4727 (18)	C8—H8A	0.959 (14)
O1—C2	1.4192 (17)	C8—H8B	1.023 (14)
O1—C3	1.4224 (17)	C9—C3^{i}	1.488 (2)
O2—C6	1.4201 (17)	C9—H9A	0.973 (13)
O2—C5	1.4308 (17)	C9—H9B	1.020 (13)
O3—C8	1.4230 (17)	C10—C11	1.417 (2)
O3—C9	1.4275 (17)	C10—C10^{ii}	1.421 (3)
C1—C2	1.503 (2)	C10—C14	1.4235 (19)
C1—H1A	0.971 (13)	C11—C12	1.361 (2)
C1—H1B	1.010 (13)	C11—H11	0.923 (13)
C2—H2A	0.995 (14)	C12—N2	1.347 (2)
C2—H2B	0.976 (14)	C12—H12	0.969 (14)
C3—C9^{i}	1.488 (2)	N2—C13	1.352 (2)
C3—H3A	0.997 (14)	C13—C14	1.362 (2)
C3—H3B	0.976 (14)	C13—H13	0.971 (14)
C4—C5	1.500 (2)	C14—H14	0.947 (12)
O3—K—O3^{i}	128.85 (4)	C9^{i}—C3—H3A	110.9 (7)
O3—K—O2	94.38 (3)	O1—C3—H3B	110.9 (8)
O3^{i}—K—O2	131.86 (3)	C9^{i}—C3—H3B	110.7 (8)
O3—K—O2^{i}	131.86 (3)	H3A—C3—H3B	106.7 (11)
O3^{i}—K—O2^{i}	94.38 (3)	N1—C4—C5	113.52 (13)
O2—K—O2^{i}	61.07 (4)	N1—C4—H4A	108.6 (8)
O3—K—O1	103.18 (3)	C5—C4—H4A	108.8 (8)
O3^{i}—K—O1	59.46 (3)	N1—C4—H4B	109.9 (8)
O2—K—O1	94.69 (3)	C5—C4—H4B	108.4 (8)

O2^{i}—K—O1	118.50 (3)	H4A—C4—H4B	107.5 (11)
O3—K—O1^{i}	59.46 (3)	O2—C5—C4	109.12 (14)
O3^{i}—K—O1^{i}	103.18 (3)	O2—C5—H5A	106.8 (8)
O2—K—O1^{i}	118.50 (3)	C4—C5—H5A	110.9 (8)
O2^{i}—K—O1^{i}	94.69 (3)	O2—C5—H5B	110.7 (8)
O1—K—O1^{i}	142.13 (4)	C4—C5—H5B	111.2 (7)
O3—K—N1^{i}	118.25 (3)	H5A—C5—H5B	108.0 (11)
O3^{i}—K—N1^{i}	61.38 (3)	O2—C6—C6^{i}	110.50 (11)
O2—K—N1^{i}	120.56 (3)	O2—C6—H6A	108.7 (8)
O2^{i}—K—N1^{i}	60.19 (3)	C6^{i}—C6—H6A	107.8 (8)
O1—K—N1^{i}	120.48 (3)	O2—C6—H6B	109.8 (7)
O1^{i}—K—N1^{i}	59.24 (3)	C6^{i}—C6—H6B	112.1 (8)
O3—K—N1	61.38 (3)	H6A—C6—H6B	107.9 (10)
O3^{i}—K—N1	118.25 (3)	N1—C7—C8	114.54 (14)
O2—K—N1	60.19 (3)	N1—C7—H7A	109.3 (7)
O2^{i}—K—N1	120.56 (3)	C8—C7—H7A	108.1 (7)
O1—K—N1	59.24 (3)	N1—C7—H7B	110.0 (7)
O1^{i}—K—N1	120.48 (3)	C8—C7—H7B	108.8 (7)
N1^{i}—K—N1	179.25 (5)	H7A—C7—H7B	105.6 (11)
C4—N1—C7	110.68 (12)	O3—C8—C7	109.67 (13)
C4—N1—C1	109.04 (12)	O3—C8—H8A	110.5 (8)
C7—N1—C1	109.81 (12)	C7—C8—H8A	109.4 (8)
C4—N1—K	109.68 (9)	O3—C8—H8B	108.3 (8)
C7—N1—K	106.11 (9)	C7—C8—H8B	113.0 (7)
C1—N1—K	111.50 (8)	H8A—C8—H8B	106.0 (11)
C2—O1—C3	112.19 (11)	O3—C9—C3^{i}	108.95 (13)
C2—O1—K	114.27 (8)	O3—C9—H9A	109.1 (7)
C3—O1—K	114.94 (9)	C3^{i}—C9—H9A	109.7 (7)
C6—O2—C5	110.94 (11)	O3—C9—H9B	108.5 (8)
C6—O2—K	113.21 (8)	C3^{i}—C9—H9B	111.9 (8)
C5—O2—K	115.81 (9)	H9A—C9—H9B	108.6 (11)
C8—O3—C9	111.28 (11)	C11—C10—C10^{ii}	123.05 (17)
C8—O3—K	116.55 (9)	C11—C10—C14	112.88 (14)
C9—O3—K	114.21 (9)	C10^{ii}—C10—C14	124.07 (16)
N1—C1—C2	113.50 (13)	C12—C11—C10	121.13 (16)
N1—C1—H1A	106.9 (7)	C12—C11—H11	118.5 (8)
C2—C1—H1A	108.0 (7)	C10—C11—H11	120.3 (8)
N1—C1—H1B	110.9 (7)	N2—C12—C11	126.20 (16)

C2—C1—H1B	108.1 (7)	N2—C12—H12	116.4 (9)
H1A—C1—H1B	109.3 (11)	C11—C12—H12	117.3 (9)
O1—C2—C1	108.45 (13)	C12—N2—C13	112.78 (15)
O1—C2—H2A	108.0 (8)	N2—C13—C14	126.02 (17)
C1—C2—H2A	109.9 (8)	N2—C13—H13	116.1 (8)
O1—C2—H2B	111.6 (8)	C14—C13—H13	117.9 (8)
C1—C2—H2B	110.2 (8)	C13—C14—C10	120.96 (16)
H2A—C2—H2B	108.6 (12)	C13—C14—H14	119.1 (8)
O1—C3—C9^{i}	108.66 (13)	C10—C14—H14	119.9 (8)
O1—C3—H3A	109.0 (7)		

Symmetry codes: (i) -*x*+3/2, *y*, -*z*+1/2; (ii) -*x*, -*y*+1, -*z*.

Literature:

[1] M. S. Denning, M. Irwin, J. M. Goicoechea, *Inorg. Chem.* **2008**, *47*, 6118-6120.
[2] C. R. Smith, *J. Am. Chem. Soc.* **1924**, *46*, 414-419.