# **Supplementary Information**

# Extending lead-free organic-inorganic semiconducting materials to new polymeric structures: 2,2'-bipyridinium iodoantimonate and quinoxalinium iodobismuthate

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**Table S2.** Hydrogen bonds geometry (Å,  $^{\circ}$ ) for the compound 1.

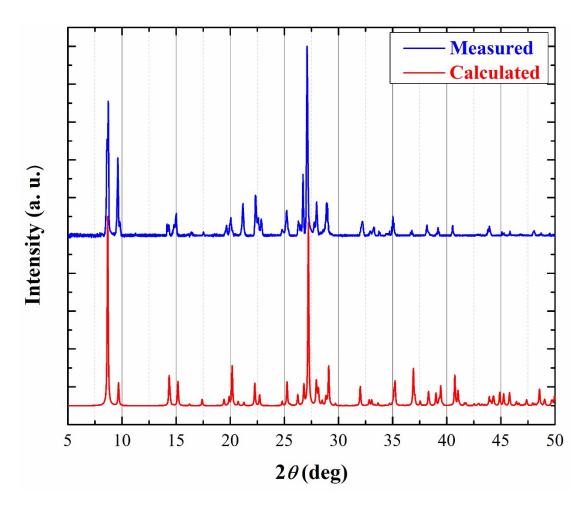
**Table S3.** Selected interatomic distances (Å) and angles (°) in the (Qx-H<sup>+</sup>) cation and MeOH of **2**.

**Table S4.** Hydrogen bonds geometry (Å, °) for the compound **2**.

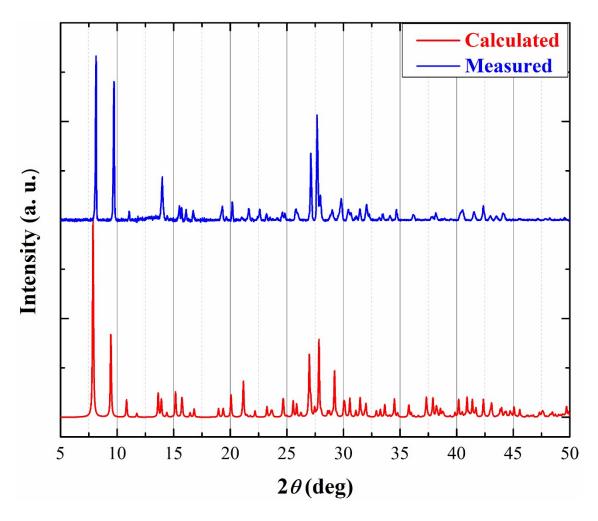
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**Table S6.** Frequencies (cm<sup>-1</sup>) of the observed Raman and infrared bands of **2** and proposed assignments.

### References



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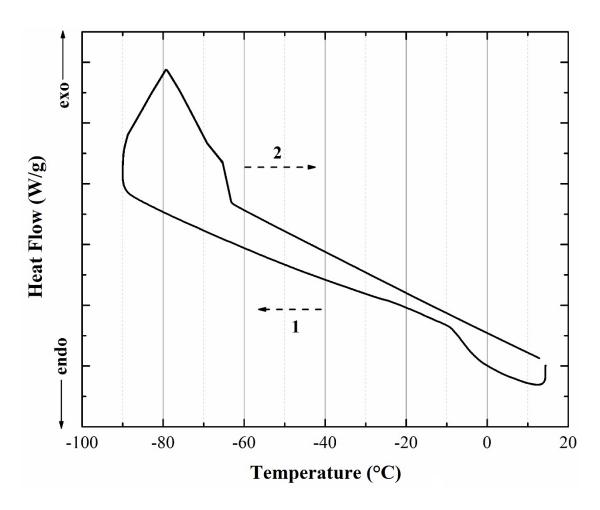


Figure S3. DSC curve for 1 at the rate of 5 °C/min upon cooling and heating.

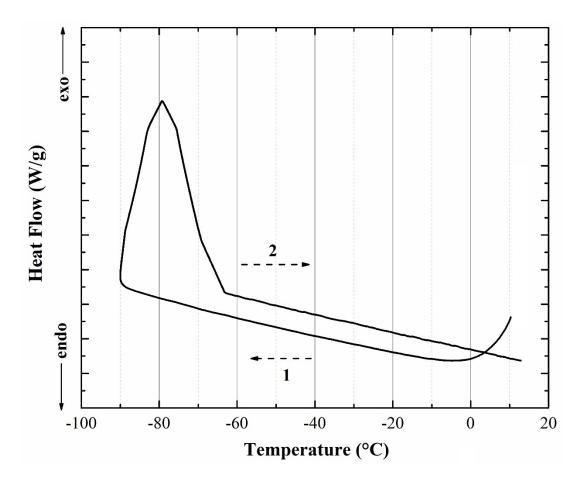
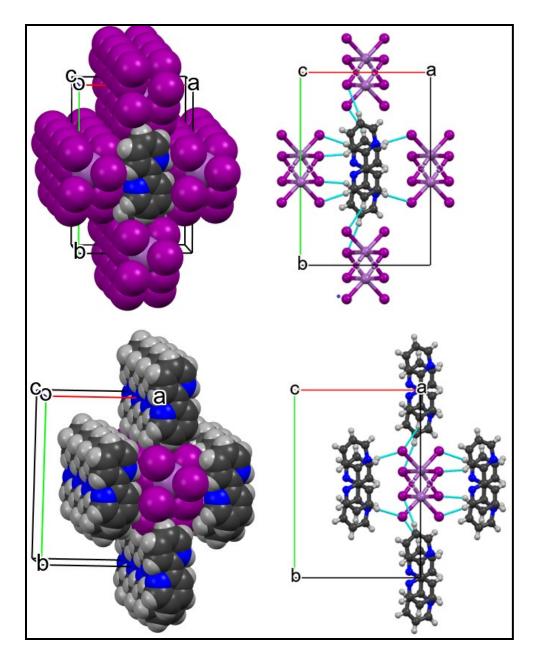
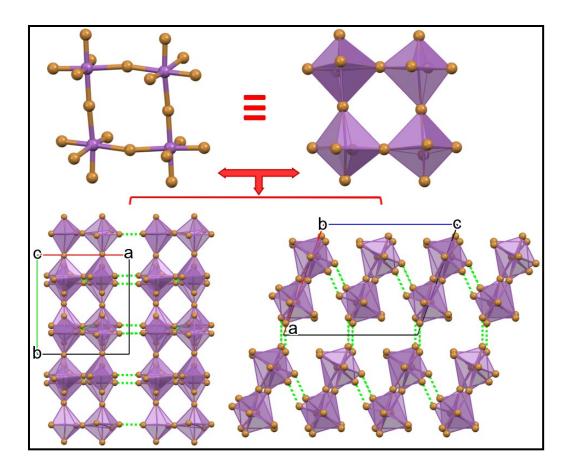


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**Figure S5.** Illustration of H-bond contacts in compound 1 (dashed lines) between anionic 1D chains and 2,2'-bipyridinium cations showing  $H\cdots I$  (<3.10 Å) interactions between molecular units.



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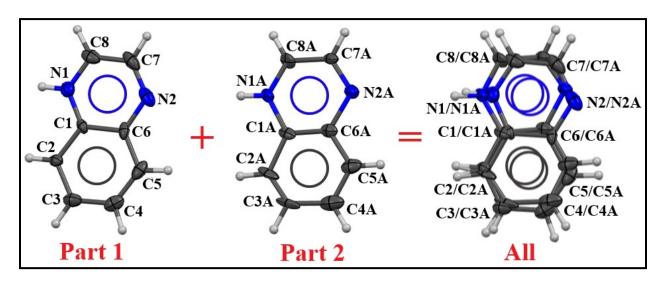
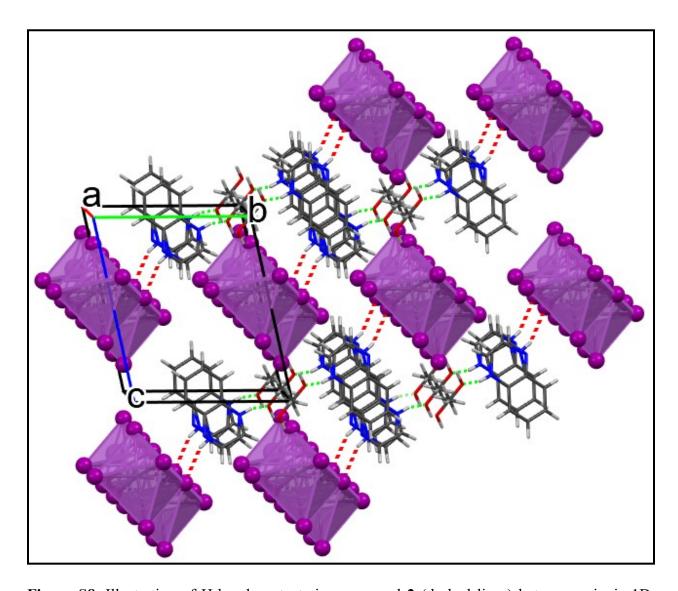


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**Figure S8.** Illustration of H-bond contacts in compound **2** (dashed lines) between anionic 1D chains, MeOH molecules and quinoxalinium cations showing H···I and H···O (<3.10 Å) interactions between molecular units.

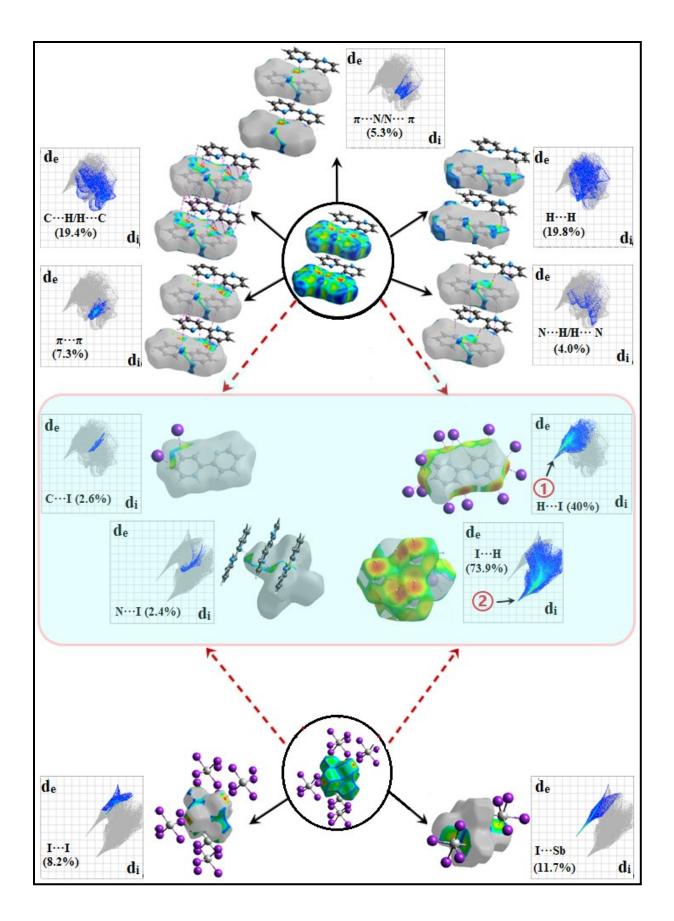
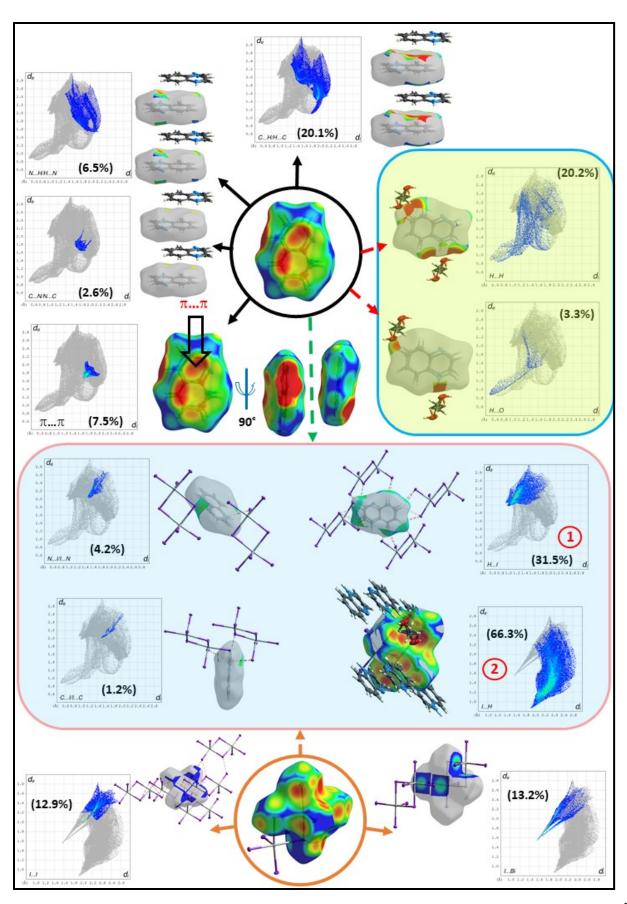


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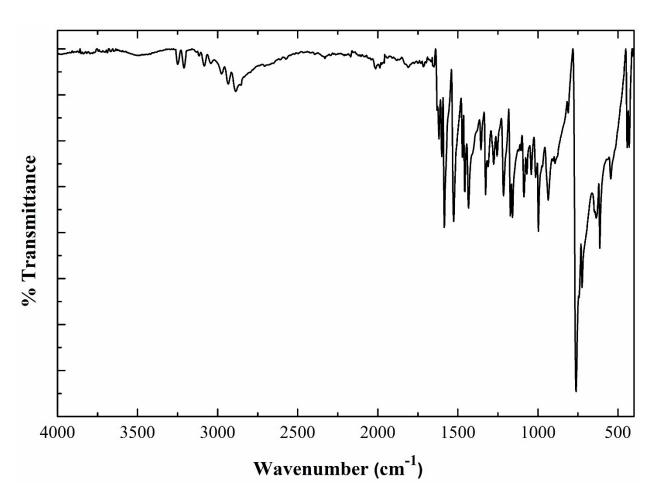


Figure S11. IR spectrum at room temperature for 1

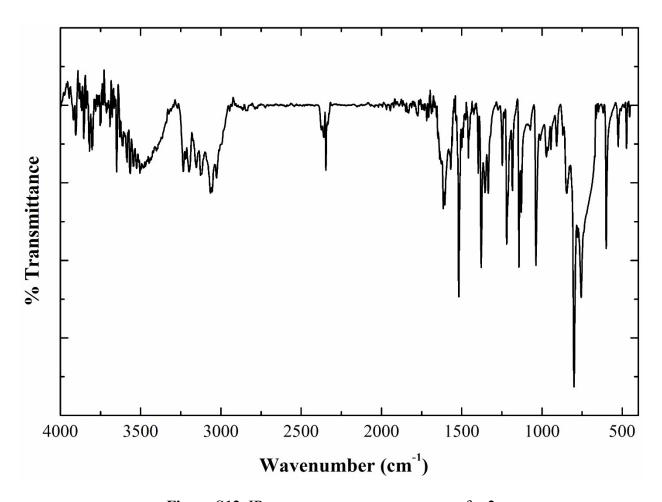


Figure S12. IR spectrum at room temperature for 2

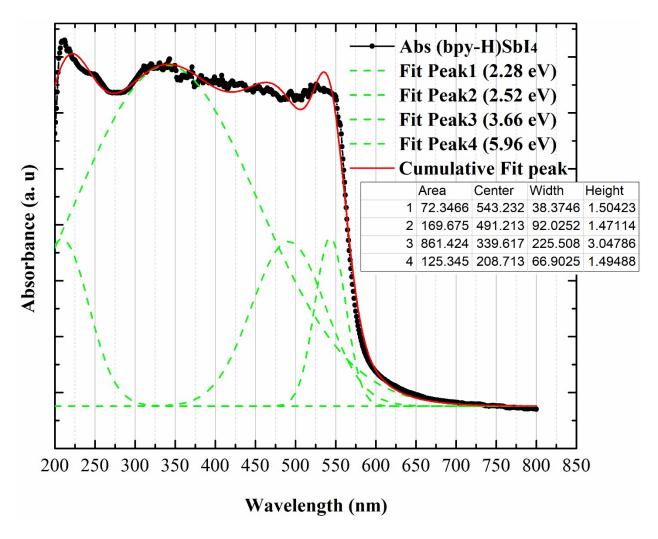
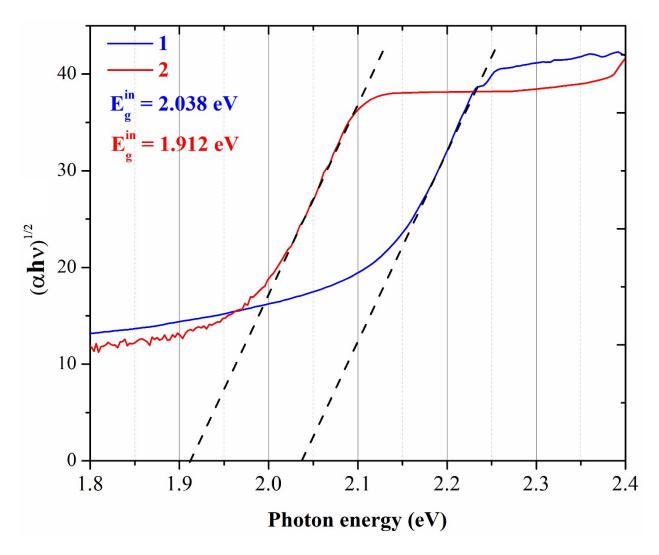


Figure S13. UV-Vis absorption spectra for 1 measured and their Gaussian decomposition.



**Figure S14.** Tauc plots of the absorbance data for an indirect allowed transition in **1** and **2**. Fits to the linear portions of the plots give the indirect bandgaps as 2.038 eV for **1** and 1.912 eV for **2**.

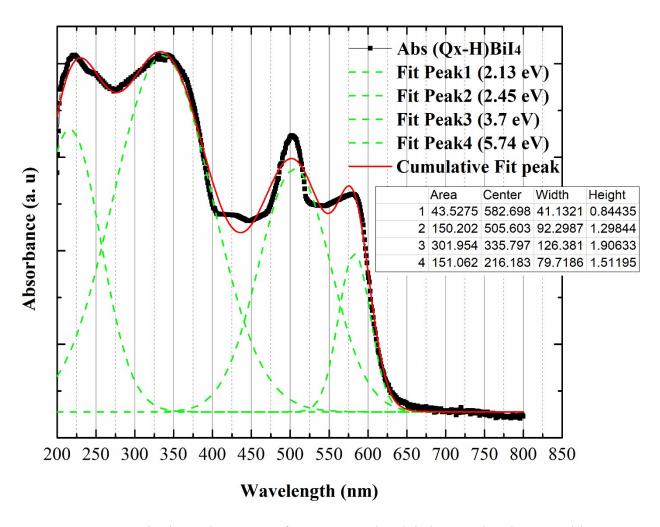


Figure S15. UV-Vis absorption spectra for 2 measured and their Gaussian decomposition.

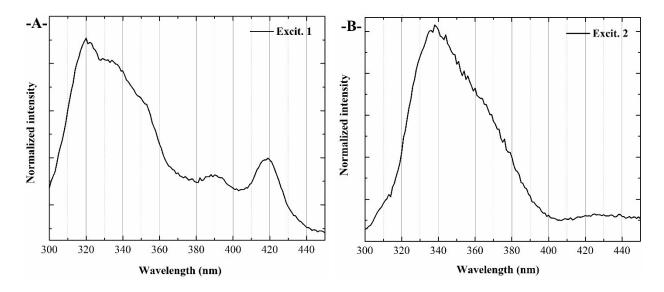


Figure S16. Normalized excitation spectra of (A) 1 ( $\lambda_{em}$  = 470 nm) and (B) 2 ( $\lambda_{em}$  = 460 nm) recorded in CH<sub>3</sub>CN at 298 K.

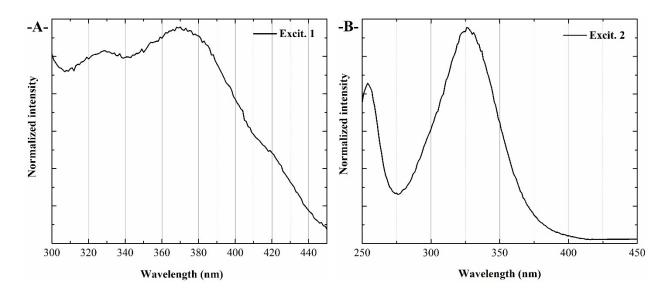
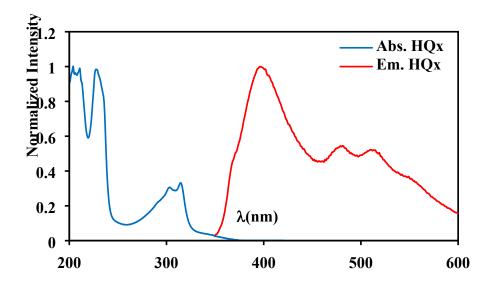


Figure S17. Normalized excitation spectra of (A) 1 ( $\lambda_{em}$  = 530 nm) and (B) 2 ( $\lambda_{em}$  = 450 nm) recorded in solid-state at 298 K.



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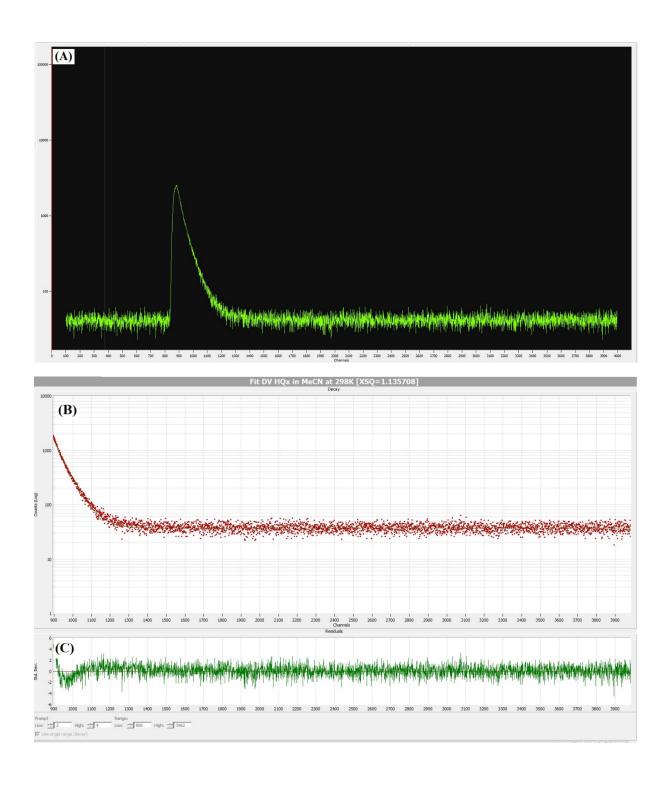
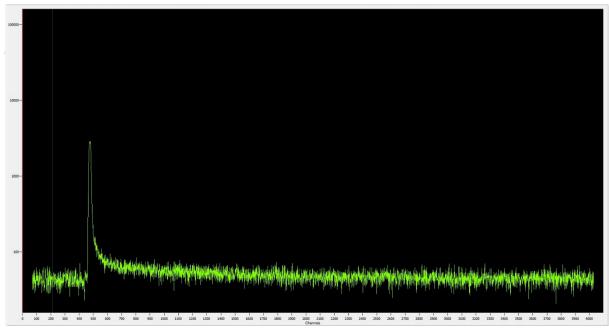


Figure S19. (A) Emission decay, (B) best fit and (C) residuals of (Qx-H)Cl in CH<sub>3</sub>CN at rt;  $\chi^2 = 1.135$ .



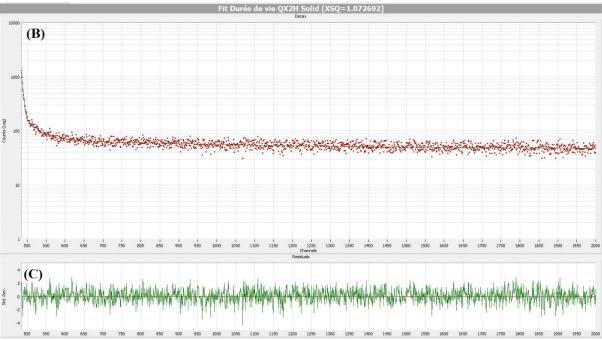


Figure S20. (A) Emission decay, (B) best fit and (C) residuals of (Qx-H)Cl in solid-state at rt;  $\chi^2 = 1.072$ .

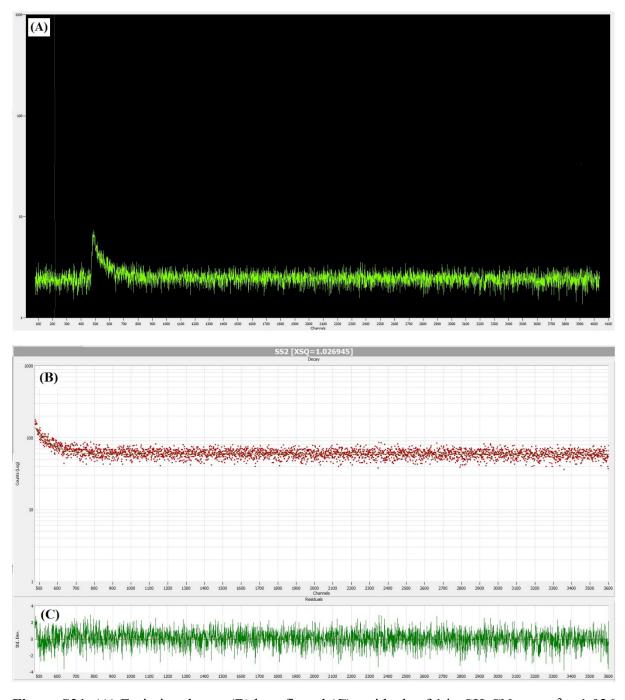
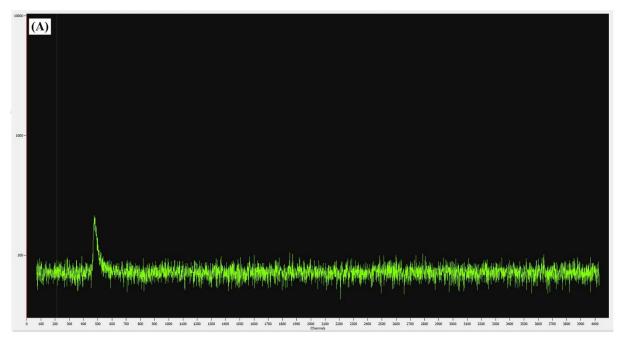


Figure S21. (A) Emission decay, (B) best fit and (C) residuals of 1 in CH<sub>3</sub>CN at rt;  $\chi^2 = 1.026$ .



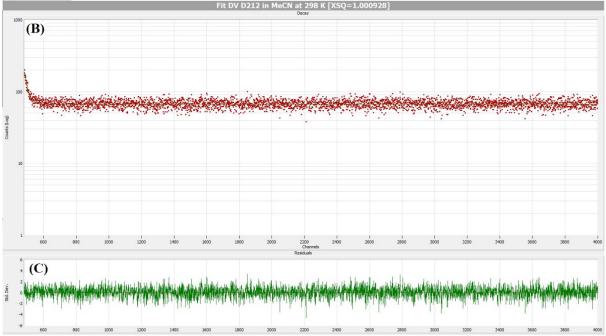
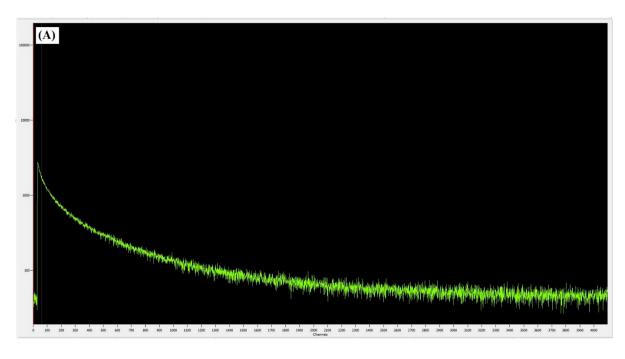


Figure S22. (A) Emission decay, (B) best fit and (C) residuals of 2 in CH<sub>3</sub>CN at rt;  $\chi^2 = 1.000$ .



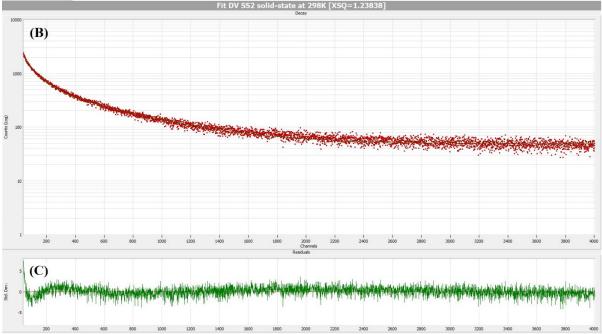


Figure S23. (A) Emission decay, (B) best fit and (C) residuals of 1 in solid-state at rt;  $\chi^2 = 1.238$ 

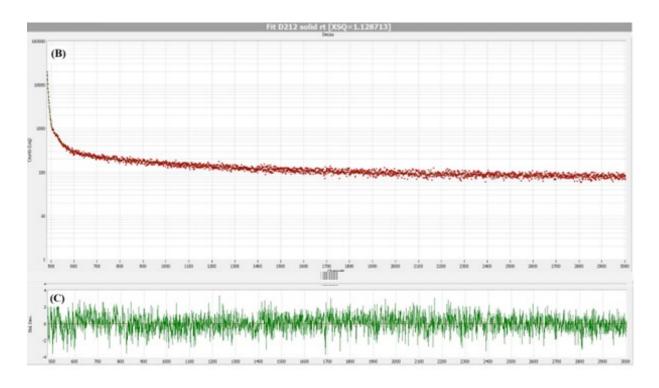


Figure S24. (A) Emission decay, (B) best fit and (C) residuals of 2 in solid-state at rt;  $\chi^2 = 1.128$ .

**Table S1.** Selected interatomic distances (Å) and angles (°) in the (bpy-H $^+$ ) cation of 1.

Bond length (Å)		Bond angles (°)	
N1—H1	0.8800	C1—N1—H1	120.9
N1—C1	1.433 (7)	C5—N1—H1	120.9
N1—C5	1.313 (13)	C5—N1—C1	118.3 (6)
N2—C6	1.444 (13)	C10—N2—C6	114.5 (7)
N2—C10	1.302 (13)	N1—C1—H1A	119.5
C1—H1A	0.9500	C2—C1—N1	121.0 (5)
C1—C2	1.389 (7)	C2—C1—H1A	119.5
C2—H2	0.9500	C1—C2—H2	120.0
C2—C3	1.370 (7)	C3—C2—C1	119.9 (5)
C3—H3	0.9500	C3—C2—H2	120.0
C3—C4	1.372 (7)	C2—C3—H3	119.6
C4—H4	0.9500	C2—C3—C4	120.8 (5)
C4—C5	1.476 (15)	C4—C3—H3	119.6
C5—C6	1.479 (4)	C3—C4—H4	121.0
C6—C7	1.279 (13)	N2—C10—H10	116.9
C7—H7	0.9500	C9—C10—H10	116.9
C7—C8	1.397 (11)	N2—C10—C9	126.1 (8)
C8—H8	0.9500	N1—C5—C6	127.6 (11)
C8—C9	1.438 (12)	C4—C5—C6	109.7 (9)
C9—H9	0.9500	N2—C6—C5	114.3 (10)
C9—C10	1.347 (14)	C3—C4—C5	118.1 (5)
C10—H10	0.9500	C5—C4—H4	121.0
		N1—C5—C4	121.1 (5)
		C7—C6—N2	123.6 (3)
		C7—C6—C5	122.1 (10)
		C6—C7—H7	119.6
		C6—C7—C8	120.7 (7)
		C8—C7—H7	119.6
		C7—C8—H8	121.6
		C7—C8—C9	116.8 (7)
		C9—C8—H8	121.6
		C8—C9—H9	121.2
		C10—C9—C8	117.6 (4)
		C10—C9—H9	121.2

**Table S2.** Hydrogen bonds geometry (Å,  $^{\circ}$ ) for the compound 1.

<i>D</i> —H···A	<i>D</i> —H	H···A	<b>D</b> ···A	<i>D</i> —H··· <i>A</i>
N1—H1···I4 <sup>iii</sup>	0.88	3.23	4.100 (5)	171
$C2$ — $H2$ ··· $I4^{iv}$	0.95	3.12	4.034 (6)	163
C4—H4···I1	0.95	2.88	3.673 (5)	142
C7—H7…I4 <sup>iii</sup>	0.95	3.22	4.152 (8)	168
C9—H9···I2 <sup>v</sup>	0.95	3.23	3.942 (7)	134
C9—H9···I3 <sup>v</sup>	0.95	3.11	3.890 (6)	140
C10—H10····I2 <sup>vi</sup>	0.95	3.16	4.082 (9)	164

*Symmetry codes:* (iii) x+1, y, z; (iv) x+1/2, -y+1/2, z-1/2; (v) x+1/2, y+1/2, z; (vi) x, -y+1, z-1/2.

**Table S3.** Selected interatomic distances (Å) and angles ( $^{\circ}$ ) in the (Qx-H $^{+}$ ) cation and MeOH of **2**.

Bond length (Å)		Bond angles (°)	
O1—H1B	0.9400	C9—O1—H1B	109.5
	0.8400		
O1—C9	1.414 (14)	O1—C9—H9A	109.5
C9—H9A	0.9800	O1—C9—H9B	109.5
C9—H9B	0.9800	O1—C9—H9C	109.5
C9—H9C	0.9800	H9A—C9—H9B	109.5
N1—H1	0.8800	H9A—C9—H9C	109.5
N1—C1	1.346 (13)	H9B—C9—H9C	109.5
N1—C8	1.324 (10)	C1—N1—H1	119.6
N2—C6	1.346 (12)	C8—N1—H1	119.6
N2—C7	1.305 (13)	C8—N1—C1	120.7 (7)
C1—C2	1.430 (13)	C7—N2—C6	120.6 (7)
C1—C6	1.421 (9)	N1—C1—C2	118.2 (10)
C2—H2	0.91 (7)	N1—C1—C6	119.1 (8)
C2—C3	1.369 (11)	C6—C1—C2	122.6 (12)
С3—Н3	0.9500	C1—C2—H2	122 (5)
C3—C4	1.417 (12)	C3—C2—C1	116.2 (13)
C4—H4	0.97 (6)	C3—C2—H2	121 (5)
C4—C5	1.386 (13)	C2—C3—H3	118.9
C5—H5	0.96 (8)	C2—C3—C4	122.2 (12)
C5—C6	1.415 (10)	C4—C3—H3	118.9
C7—H7	0.96 (8)	C3—C4—H4	116 (4)
C7—C8	1.390 (12)	C5—C4—C3	122.0 (12)
C8—H8	1.03 (7)	C5—C4—H4	122 (4)
N1A—H1A	0.8800	C4—C5—H5	127 (5)
N1A—C1A	1.39 (4)	C4—C5—C6	117.9 (10)

N1A—C8A				
N2A—C7A  1.29 (2)  N2—C6—C5  1122.3 (7)  C1A—C2A  1.39 (3)  C5—C6—C1  119.1 (9)  C1A—C6A  1.37 (3)  N2—C7—H7  122 (5)  C2A—H2A  0.9500  N2—C7—C8  121.4 (7)  C2A—C3A  1.33 (3)  C8—C7—H7  117 (5)  C3A—H3A  0.9500  N1—C8—C7  119.4 (8)  C3A—C4A  1.38 (3)  N1—C8—H8  115 (4)  C4A—H4A  0.9500  C7—C8—H8  125 (4)  C4A—C5A  1.35 (3)  C1A—N1A—H1A  119.7  C5A—H5A  0.9500  C8A—N1A—H1A  119.7  C5A—C6A  1.37 (2)  C8A—N1A—C1A  121 (2)  C7A—H7A  0.9500  C7A—N2A—C6A  115 (2)  C7A—C8A  1.40 (2)  N1A—C1A—C2A  132 (4)  C8A—H8A  0.9500  C6A—C1A—N1A  117 (3)  C6A—C1A—C2A  111 (4)  C1A—C2A—H2A  115.8  C3A—C2A—H2A  115.8  C2A—C3A—H3A  120.6  C3A—C4A—H4A  122.4  C5A—C4A—C3A  115 (4)  C4A—C5A—C6A  125 (3)  C6A—C5A—H5A  117.7  C4A—C5A—C6A  125 (3)  C6A—C5A—H5A  117.7  C4A—C5A—H5A  117.7  C4A—C5A—C6A  122 (2)  C1A—C6A—N2A  112 (2)  C1A—C6A—N2A  112 (2)  C1A—C6A—N2A  112 (2)  C1A—C6A—N2A  112 (2)  C1A—C6A—N2A  118.9  N2A—C7A—H7A  118.9  N2A—C7A—H7A  118.9  N1A—C8A—H8A  118.7	N1A—C8A	1.29 (3)	C6—C5—H5	114 (5)
C1A—C2A C1A—C6A C1A—C6A C1A—C6A C2A—H2A C2A—H2A C2A—C3A C3A C3A C3A C3A—C4A C4A—C5A C5A—C6A C5A—C6A C7—H7 C5A—C6A C7A—C7A C7A—C8 C7A—C7A—C8 C7A—C8 C7A—C7A—C8 C7A—C7A—C8 C7A—C7A—C8 C7A—C7A—C7A—C8 C7A—C7A—C7A—C8 C7A—C7A—C7A—C7A—C7A—C7A—C7A—C7A—C7A—C7A—	N2A—C6A	1.47 (3)	N2—C6—C1	118.6 (8)
C1A—C6A C2A—H2A C2A—H2A C2A—C3A C3A—H3A C3A—H3A C3A—H3A C4A—H3A C5A—C4A C5A—C5A C5A—H5A C5A—H5A C5A—H5A C6A—C1A—H7A C6A—C1A—H1A C1A—C6A—C1A C1B—C6A—C1A C1B—C6A—C1A C1B—C6A—C1A C1B—C6A—C1A C1B—C6A—C1A C1B—C6A—C5A C1B—C6A—C5A C1B—C6A—C1A C1B—C6A—C1A C1B—C6A—C5A C1B—C6A—C1A C1B—C6A—C1A C1B—C6A—C1A C1B—C6A—C1A C1B—C1A—C1A C1B—C1A—C1A—C1A C1B—C1A—C1A C1B—C1A—C1A—C1A C1B—C1A—C1A C1B—C1A—C1A—C1A C1B—C1A—C1A C1B—C1A—C1A—C1A C1B—C1B—C1B—C1B C1B—C1B—C1B—C1B C1B—C1B—C1B—C1B C1B—C1B—C1B—C1B C1B—C1B—C1B—C1B C1B—C1	N2A—C7A	1.29 (2)	N2—C6—C5	122.3 (7)
C2A—H2A         0.9500         N2—C7—C8         121.4 (7)           C2A—C3A         1.33 (3)         C8—C7—H7         117 (5)           C3A—H3A         0.9500         N1—C8—C7         119.4 (8)           C3A—C4A         1.38 (3)         N1—C8—H8         115 (4)           C4A—C5A         1.35 (3)         C1A—N1A—H1A         119.7           C5A—H5A         0.9500         C8A—N1A—H1A         119.7           C5A—C6A         1.37 (2)         C8A—N1A—C1A         121 (2)           C7A—H7A         0.9500         C7A—N2A—C6A         115 (2)           C7A—C8A         1.40 (2)         N1A—C1A—C2A         132 (4)           C8A—H8A         0.9500         C6A—C1A—N1A         117 (3)           C6A—C1A—C2A         111 (4)         C1A—C2A—H2A         115.8           C3A—C2A—H2A         115.8         C3A—C2A—H2A         115.8           C3A—C2A—H2A         115.8         C2A—C3A—H3A         120.6           C3A—C4A—H4A         122.4         C5A—C4A—H4A         122.4           C5A—C4A—H3A         119 (4)         C4A—C5A—H5A         117.7           C4A—C5A—H5A         117.7         C1A—C6A—N2A         122 (3)           C5A—C6A—N2A         116 (2)         N2A—C7A	C1A—C2A	1.39 (3)	C5—C6—C1	119.1 (9)
C2A—C3A         1.33 (3)         C8—C7—H7         117 (5)           C3A—H3A         0.9500         N1—C8—C7         119.4 (8)           C3A—C4A         1.38 (3)         N1—C8—H8         115 (4)           C4A—H4A         0.9500         C7—C8—H8         125 (4)           C4A—C5A         1.35 (3)         C1A—N1A—H1A         119.7           C5A—H5A         0.9500         C8A—N1A—H1A         119.7           C5A—C6A         1.37 (2)         C8A—N1A—C1A         121 (2)           C7A—H7A         0.9500         C7A—N2A—C6A         115 (2)           C7A—C8A         1.40 (2)         N1A—C1A—C2A         132 (4)           C8A—H8A         0.9500         C6A—C1A—N1A         117 (3)           C6A—C1A—C2A         111 (4)         C1A—C2A—H2A         115.8           C3A—C2A—H2A         115.8         C3A—C2A—H2A         115.8           C3A—C2A—H2A         115.8         C2A—C3A—C4A         119 (4)           C4A—C3A—H3A         120.6         C3A—C4A—H4A         122.4           C5A—C4A—H4A         122.4         C4A—C5A—H5A         117.7           C4A—C5A—H5A         117.7         C1A—C6A—C3A         115 (4)           C5A—C4A—H5A         117.7         C1A—C6A—C5A	C1A—C6A	1.37 (3)	N2—C7—H7	122 (5)
C3A—H3A C3A—C4A C3A—C4A C3A—C4A C4A—H4A C4A—H4A C5A—C5A C5A—C6A C5A—C6A C7—C8—H8 C7—C8—H8 C7—C8—H8 C7—C8—H8 C7—C8—H8 C7—C8—H8 C7—C8—H8 C7—C8—H8 C8A—N1A—N1A C8A—N1A—N1A C8A—C6A C9500 C8A—N1A—H1A C9500 C7A—N2A—C6A C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C7A—C8A C7A—C7A—C7A—C7A—C7A—C7A—C7A—C7A—C7A—C7A—	C2A—H2A	0.9500	N2—C7—C8	121.4 (7)
C3A—C4A C4A—H4A C4A—H4A C4A—H4A C5A C4A—C5A C5A—H5A C5A—H5A C5A—C6A C7A—H7A C7A—H7A C7A—C8A C8A—H8A C8A—H8A C9500 C8A—N1A—H1A C7A—C6A C7A—H7A C9500 C7A—N2A—C6A C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C8A C7A—C7A—C7A C7A—C8A C7A—C7A—C7A C7A—C7A—C7A—C7A C7A—C7A—C7A—C7A C7A—C7A—C7A—C7A C7A—C7A—C7A—C7A—C7A C7A—C7A—C7A—C7A—C7A—C7A—C7A—C7A—C7A—C7A—	C2A—C3A	1.33 (3)	C8—C7—H7	117 (5)
C4A—H4A C4A—C5A C4A—C5A C4A—C5A C5A—C6A C5A—C6A C5A—C6A C7A—T7A C5A—C6A C6A—C1A—C1A—C1A C6A—C1A—C2A C6A—C1A—C2A C1A—C2A—C1A C2A—C3A—C4A—C4A C2A—C3A—C4A—C4A—C5A C3A—C4A—H4A C4A—C5A—H5A C1A—C5A—C6A C1A—C4A—C5A—C6A C1A—C4A—C5A—C6A C1A—C4A—C5A—C6A C1A—C5A—C6A—C1A—C5A C1A—C5A—C6A—C1A—C5A C1A—C5A—C6A—C1A—C5A C1A—C5A—C6A—C1A—C5A C1A—C5A—C6A—C1A—C5A C1A—C5A—C6A—C1A—C5A C1A—C5A—C6A—C1A—C5A—C6A—C1A—C5A—C6A—C1A—C5A—C6A—C1A—C5A—C6A—C1A—C5A—C6A—C1A—C5A—C6A—C1A—C5A—C6A—C1A—C5A—C6A—C1A—C5A—C6A—C6A—C6A—C6A—C6A—C6A—C6A—C6A—C6A—C6	C3A—H3A	0.9500	N1—C8—C7	119.4 (8)
C4A—C5A C5A—H5A C5A—H5A C5A—H5A C5A—C6A C5A—C6A C7A—H7A C5A—C6A C7A—H7A C5A—C8A C8A—N1A—C1A C1B—C2A C8A—H8A  C1A—C2A C1A—C2A C11C C7A—H8A  C1A—C2A—C1A C1B—C2A C1B—C2A—C1A C2A—C1A C1B—C6A C2A—C3A—C4A C3A—C4A—C3A C4A—C5A—H4A C5A—C4A—C3A C4A—C5A—H5A C4A—C5A—H5A C4A—C5A—H5A C1A—C6A—C5A C1C C1A—C6A—C6A C1C C1C C1C C1C C1C C1C C1C C1C C1C C1	C3A—C4A	1.38 (3)	N1—C8—H8	115 (4)
C5A—H5A C5A—C6A C5A—C6A C5A—C6A C7A—H7A C9500 C7A—N2A—C6A C7A—C8A C8A—N1A—C1A C8A—N1A—C1A C8A—H8A C8A—H8A C9500 C6A—C1A—C2A C1A—C2A C11 (4) C1A—C2A—H14 C1A—C2A C11 (5) C3A—C2A—C1A C11 (4) C1A—C2A—H2A C13 (5) C3A—C2A—C1A C2A—C1A C2A—C1A C2A—C1A C2A—C1A C2A—H2A C2A—C3A—H3A C2A—C3A—H3A C3A—C4A—H4A C3A—C4A—H4A C4A—C3A—H4A C5A—C4A—H4A C5A—C4A—H4A C5A—C4A—H4A C5A—C4A—H4A C5A—C4A—H4A C5A—C4A—H4A C5A—C4A—H4A C5A—C5A—H5A C1A—C5A—H5A C1A—C6A—N2A C1A—C6A—N2	C4A—H4A	0.9500	C7—C8—H8	125 (4)
C5A—C6A       1.37 (2)       C8A—N1A—C1A       121 (2)         C7A—H7A       0.9500       C7A—N2A—C6A       115 (2)         C7A—C8A       1.40 (2)       N1A—C1A—C2A       132 (4)         C8A—H8A       0.9500       C6A—C1A—N1A       117 (3)         C6A—C1A—C2A       111 (4)       C1A—C2A—H2A       115.8         C3A—C2A—H2A       115.8       C3A—C2A—H2A       115.8         C2A—C3A—H3A       120.6       C2A—C3A—H3A       120.6         C2A—C3A—H3A       120.6       C3A—C4A—H4A       122.4         C5A—C4A—H4A       122.4       C5A—C4A—H4A       122.4         C4A—C5A—H5A       117.7       C4A—C5A—H5A       117.7         C1A—C6A—N2A       125 (3)       C6A—C5A—H5A       117.7         C1A—C6A—N2A       122 (2)       C1A—C6A—C5A       122 (3)         C5A—C6A—N2A       116 (2)       N2A—C7A—H7A       118.9         N2A—C7A—H7A       118.9       N1A—C8A—C7A       123 (2)         N1A—C8A—C7A       123 (2)       N1A—C8A—H8A       118.7	C4A—C5A	1.35 (3)	C1A—N1A—H1A	119.7
C7A—H7A       0.9500       C7A—N2A—C6A       115 (2)         C7A—C8A       1.40 (2)       N1A—C1A—C2A       132 (4)         C8A—H8A       0.9500       C6A—C1A—N1A       117 (3)         C6A—C1A—C2A       111 (4)       115.8         C3A—C2A—H2A       115.8       128 (5)         C3A—C2A—H2A       115.8       115.8         C2A—C3A—H3A       120.6       119 (4)         C4A—C3A—H3A       120.6       119 (4)         C3A—C4A—H4A       122.4       115 (4)         C5A—C4A—H4A       122.4       117.7         C4A—C5A—H5A       117.7       117.7         C4A—C5A—H5A       117.7       117.7         C1A—C6A—N2A       122 (2)       122 (2)         C1A—C6A—C5A       122 (3)       116 (2)         N2A—C7A—H7A       118.9       N2A—C7A—C8A       122.3 (18)         C8A—C7A—H7A       118.9       N1A—C8A—H8A       118.7	C5A—H5A	0.9500	C8A—N1A—H1A	119.7
C7A—C8A       1.40 (2)       N1A—C1A—C2A       132 (4)         C8A—H8A       0.9500       C6A—C1A—N1A       117 (3)         C6A—C1A—C2A       111 (4)       115.8         C1A—C2A—H2A       115.8       128 (5)         C3A—C2A—H2A       115.8       115.8         C2A—C3A—H3A       120.6       120.6         C2A—C3A—H3A       120.6       119 (4)         C4A—C3A—H3A       120.6       122.4         C5A—C4A—H4A       122.4       115 (4)         C5A—C4A—H4A       122.4       117.7         C4A—C5A—H5A       117.7       117.7         C4A—C5A—C6A       125 (3)       122 (2)         C1A—C6A—N2A       122 (2)       122 (2)         C1A—C6A—N2A       116 (2)       N2A—C7A—H7A       118.9         N2A—C7A—C8A       122.3 (18)       118.9         N1A—C8A—H8A       118.7	C5A—C6A	1.37 (2)	C8A—N1A—C1A	121 (2)
C8A—H8A  0.9500  C6A—C1A—N1A  C6A—C1A—C2A  111 (4)  C1A—C2A—H2A  115.8  C3A—C2A—C1A  128 (5)  C3A—C2A—H2A  115.8  C2A—C3A—H3A  120.6  C2A—C3A—H3A  120.6  C3A—C4A—H4A  122.4  C5A—C4A—H4A  122.4  C5A—C4A—H4A  122.4  C4A—C5A—H5A  117.7  C4A—C5A—H5A  117.7  C1A—C6A—N2A  122 (2)  C1A—C6A—N2A  116 (2)  N2A—C7A—H7A  118.9  N1A—C8A—C7A  118.9  N1A—C8A—C7A  118.7	C7A—H7A	0.9500	C7A—N2A—C6A	115 (2)
C6A—C1A—C2A 111 (4) C1A—C2A—H2A 115.8 C3A—C2A—C1A 128 (5) C3A—C2A—H2A 115.8 C2A—C3A—H3A 120.6 C2A—C3A—C4A 119 (4) C4A—C3A—H3A 120.6 C3A—C4A—H4A 122.4 C5A—C4A—H4A 122.4 C5A—C4A—H4A 122.4 C4A—C5A—H5A 117.7 C4A—C5A—H5A 117.7 C4A—C5A—C6A 125 (3) C6A—C5A—H5A 117.7 C1A—C6A—N2A 122 (2) C1A—C6A—C5A 122 (3) C5A—C6A—N2A 116 (2) N2A—C7A—H7A 118.9 N2A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7	C7A—C8A	1.40(2)	N1A—C1A—C2A	132 (4)
C1A—C2A—H2A C3A—C2A—C1A C3A—C2A—H2A C3A—C3A—H3A C2A—C3A—H3A C2A—C3A—H3A C2A—C3A—H3A C3A—C4A C3A—C4A—H4A C3A—C4A—H4A C5A—C4A—C3A C4A—C5A—H5A C4A—C5A—H5A C4A—C5A—H5A C1A—C6A—N2A C1B—C6A—N2A C1B—C6A—N2	C8A—H8A	0.9500	C6A—C1A—N1A	117 (3)
C3A—C2A—C1A C3A—C2A—H2A C3A—C3A—H3A C2A—C3A—H3A C2A—C3A—C4A C3A—C4A C4A—C3A—H3A C5A—C4A—H4A C5A—C4A—H4A C5A—C4A—H5A C4A—C5A—H5A C1A—C6A—N2A C1A—C6A—N2A C1A—C6A—N2A C1A—C6A—N2A C5A—C6A—N2A C1A—C6A—N2A C5A—C6A—N2A C5A—C6A—N2A C5A—C6A—N2A C1A—C6A—N2A C5A—C6A—N2A N2A—C7A—H7A N2A—C7A—H7A N2A—C7A—H7A N18.9 N1A—C8A—C7A N1A—C8A—C7A N1A—C8A—C7A N1A—C8A—C7A N1A—C8A—C7A N1A—C8A—H8A N1A—C8A—H8A			C6A—C1A—C2A	111 (4)
C3A—C2A—H2A 115.8  C2A—C3A—H3A 120.6  C2A—C3A—C4A 119 (4)  C4A—C3A—H3A 120.6  C3A—C4A—H4A 122.4  C5A—C4A—C3A 115 (4)  C5A—C4A—H4A 122.4  C4A—C5A—H5A 117.7  C4A—C5A—H5A 117.7  C1A—C6A—N2A 122 (2)  C1A—C6A—N2A 122 (3)  C5A—C6A—N2A 116 (2)  N2A—C7A—H7A 118.9  N2A—C7A—H7A 118.9  N1A—C8A—C7A 123 (2)  N1A—C8A—C7A 123 (2)  N1A—C8A—H8A 118.7			C1A—C2A—H2A	115.8
C2A—C3A—H3A 120.6 C2A—C3A—C4A 119 (4) C4A—C3A—H3A 120.6 C3A—C4A—H4A 122.4 C5A—C4A—C3A 115 (4) C5A—C4A—H4A 122.4 C4A—C5A—H5A 117.7 C4A—C5A—C6A 125 (3) C6A—C5A—H5A 117.7 C1A—C6A—N2A 122 (2) C1A—C6A—C5A 122 (3) C5A—C6A—N2A 116 (2) N2A—C7A—H7A 118.9 N2A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			C3A—C2A—C1A	128 (5)
C2A—C3A—C4A C4A—C3A—H3A C4A—C3A—H4A C3A—C4A—H4A C5A—C4A—H4A C5A—C4A—H4A C5A—C5A—H5A C4A—C5A—H5A C1A—C5A—H5A C1A—C6A—N2A C1A—C6A—C5A C1A—C6A—N2A C5A—C6A—N2A N2A—C7A—H7A N1A—C8A—C7A—H7A N1A—C8A—C7A N1A—C8A—C7A N1A—C8A—C7A N1A—C8A—H8A N1A—C8A—H8A			C3A—C2A—H2A	115.8
C4A—C3A—H3A 120.6 C3A—C4A—H4A 122.4 C5A—C4A—C3A 115 (4) C5A—C4A—H4A 122.4 C4A—C5A—H5A 117.7 C4A—C5A—H5A 117.7 C1A—C6A—N2A 122 (2) C1A—C6A—C5A 122 (3) C5A—C6A—N2A 116 (2) N2A—C7A—H7A 118.9 N2A—C7A—C8A 122.3 (18) C8A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			C2A—C3A—H3A	120.6
C3A—C4A—H4A C5A—C4A—C3A C5A—C4A—H4A C5A—C4A—H4A C4A—C5A—H5A C4A—C5A—C6A C5A—C6A C5A—C6A—N2A C1A—C6A—N2A C1A—C6A—N2A C5A—C6A—N2A N2A—C7A—H7A N2A—C7A—C8A C8A—C7A—H7A N18.9 N1A—C8A—C7A N1A—C8A—C7A N1A—C8A—H8A N1A—C8A—H8A			C2A—C3A—C4A	119 (4)
C5A—C4A—C3A 115 (4) C5A—C4A—H4A 122.4 C4A—C5A—H5A 117.7 C4A—C5A—H5A 117.7 C1A—C6A—N2A 122 (2) C1A—C6A—C5A 122 (3) C5A—C6A—N2A 116 (2) N2A—C7A—H7A 118.9 N2A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			C4A—C3A—H3A	120.6
C5A—C4A—H4A C4A—C5A—H5A C4A—C5A—C6A C5A—C5A—H5A C1A—C6A—N2A C1A—C6A—C5A C5A—C5A—H5A C1A—C6A—C5A C1A—C6A—C5A C1A—C6A—C5A C5A—C6A—N2A C5A—C6A—N2A C5A—C6A—N2A C5A—C6A—N2A C5A—C6A—N2A C5A—C6A—N2A C5A—C6A—N2A C5A—C7A—H7A C8A—C7A—H7A C8A—C7A—H7A C8A—C7A—H7A C8A—C7A—H7A C8A—C7A—H8A C8A—C7A C8A—C7A—H8A C8A—C7A C8A—C7A—H8A			C3A—C4A—H4A	122.4
C4A—C5A—H5A 117.7 C4A—C5A—C6A 125 (3) C6A—C5A—H5A 117.7 C1A—C6A—N2A 122 (2) C1A—C6A—C5A 122 (3) C5A—C6A—N2A 116 (2) N2A—C7A—H7A 118.9 N2A—C7A—C8A 122.3 (18) C8A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			C5A—C4A—C3A	115 (4)
C4A—C5A—C6A 125 (3) C6A—C5A—H5A 117.7 C1A—C6A—N2A 122 (2) C1A—C6A—C5A 122 (3) C5A—C6A—N2A 116 (2) N2A—C7A—H7A 118.9 N2A—C7A—C8A 122.3 (18) C8A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			C5A—C4A—H4A	122.4
C6A—C5A—H5A 117.7 C1A—C6A—N2A 122 (2) C1A—C6A—C5A 122 (3) C5A—C6A—N2A 116 (2) N2A—C7A—H7A 118.9 N2A—C7A—C8A 122.3 (18) C8A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			C4A—C5A—H5A	117.7
C1A—C6A—N2A 122 (2) C1A—C6A—C5A 122 (3) C5A—C6A—N2A 116 (2) N2A—C7A—H7A 118.9 N2A—C7A—C8A 122.3 (18) C8A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			C4A—C5A—C6A	125 (3)
C1A—C6A—C5A 122 (3) C5A—C6A—N2A 116 (2) N2A—C7A—H7A 118.9 N2A—C7A—C8A 122.3 (18) C8A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			C6A—C5A—H5A	117.7
C5A—C6A—N2A 116 (2) N2A—C7A—H7A 118.9 N2A—C7A—C8A 122.3 (18) C8A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			C1A—C6A—N2A	122 (2)
N2A—C7A—H7A 118.9 N2A—C7A—C8A 122.3 (18) C8A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			C1A—C6A—C5A	122 (3)
N2A—C7A—C8A 122.3 (18) C8A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			C5A—C6A—N2A	116 (2)
C8A—C7A—H7A 118.9 N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			N2A—C7A—H7A	118.9
N1A—C8A—C7A 123 (2) N1A—C8A—H8A 118.7			N2A—C7A—C8A	122.3 (18)
N1A—C8A—H8A 118.7			C8A—C7A—H7A	118.9
			N1A—C8A—C7A	123 (2)
C7A—C8A—H8A 118.7			N1A—C8A—H8A	118.7
			C7A—C8A—H8A	118.7

**Table S4.** Hydrogen bonds geometry ( $\acute{A}$ ,  $^{\circ}$ ) for the compound **2**.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	$\mathbf{H}$ ··· $A$	<b>D</b> ····A	<i>D</i> —H··· <i>A</i>
O1—H1 <i>B</i> ···I2 <sup>iii</sup>	0.84	2.92	3.680 (11)	152
C9—H9A···I2 <sup>iv</sup>	0.98	3.27	4.04 (3)	137
C9—H9A···I3 <sup>iv</sup>	0.98	3.13	3.91 (4)	138
С9—Н9В…ІЗііі	0.98	3.20	3.88 (4)	127
C2A—H2A···I2 <sup>iv</sup>	0.95	3.12	4.05 (5)	165
C7A—H7A…I1	0.95	3.12	3.856 (17)	136
C7A—H7A···I4 <sup>v</sup>	0.95	3.17	3.849 (19)	130
C2—H2···I2 <sup>iv</sup>	0.92 (8)	3.22 (8)	4.039 (17)	149 (6)
C5—H5···I3 <sup>vi</sup>	0.98 (9)	3.23 (9)	4.195 (12)	172 (7)
C7—H7···I1 <sup>v</sup>	0.96 (9)	3.29 (9)	3.784 (19)	114 (6)
C7—H7···I4 <sup>v</sup>	0.96 (9)	3.24 (8)	3.857 (10)	124 (6)
С8—Н8…11	1.03 (7)	3.21 (7)	3.956 (10)	130 (5)
C8—H8···I4 <sup>iii</sup>	1.03 (7)	3.30 (7)	3.816 (12)	112 (4)

*Symmetry codes:* (iii) x+1, y, z; (iv) -x+1, -y+2, -z; (v) -x+1, -y+1, -z+1; (vi) x, y-1, z.

**Table S5.** Frequencies (cm<sup>-1</sup>) of the observed Raman and infrared bands of 1 and proposed assignments.

Wavenumber (cm <sup>-1</sup> )		Assignment	
Raman	Infrared		
55		Bending modes	
77			
88			
95		Sb–I <sub>(bridge)</sub> stretching	
112			
126			
156		Sb-I <sub>(external)</sub> stretching	
	423	γ(heterocyclic ring)	
	441	heterocyclic ring torsion	
	542	$\delta(CCC) + \delta(CCN)$	
	610	-()	
	635		
	718	$\gamma(C=C) + \gamma(C=N)$	
	737	((0.0))	
	761	γ(C–H)aromatic	
	811	(C 11) at official	
	935		
	998	β(C–H)aromatic	
	1008	p(C-11)aromatic	
	1035		
	1063		
	1081		
	1153		
	1166		
	1209	(C-C)  (C-N)	
	1249	v(C=C)+v(C=N)	
	1349		
	1427		
	1451		
	1465		
	1520		
	1578		
	1594		
	1612	(= ==	
	2887	ν(C–H)aromatic	
	2930		
	2974		
	3043		
	3081		
	3205	$\nu({ m NH^+})$	
	3250		

 $\frac{3250}{v: stretching, δ: deformation, β: in plane bending, γ: out of plane bending}$ 

**Table S6.** Frequencies (cm<sup>-1</sup>) of the observed Raman and infrared bands of **2** and proposed assignments.

Wavenumber (cm <sup>-1</sup> )		Assignment
Raman	Infrared	<del></del>
55		Bending modes
73		C
93		Bi–I <sub>(bridge)</sub> stretching
122		(
141		Bi-I <sub>(external)</sub> stretching
	453	δ(CCC)
	472	,
	524	δ(CCN)
	600	,
	756	$\gamma(C=C) + \gamma(C=N)$
	799	10 / 10 - 9
	844	
	869	
	906	γ(CCH)aromatic
	943	\(\(\cup \) \(\cup \) \(\c
	970	
	1037	v(C–O)methanol
	1071	(
	1129	δ(CCH)aromatic
	1141	o (e e 17) di e indica
	1184	
	1218	
	1245	
	1334	$\nu$ (C=C)
	1352	,(8 8)
	1395	
	1459	
	1517	
	1566	$v(C=NH^+)$
	1603	v(C 1111 )
	1615	
	3026	v(C–H)methanol
	3063	v(C-11)medianoi
	3125	ν(C–H)aromatic
	3123	v(C-H)aromatic
		ν(NH <sup>+</sup> )
	3197	V(INIT )
	3234	(O II)41 1
	3455	ν(O–H)methanol

## References

**1** M. D. Petrov, M. N. Sokolov, V. P. Fedin and S. A. Adonin, *J. Struct. Chem.*, 2020, **61**, 1794-1799. https://doi.org/10.1134/S0022476620110128.

**2** A. Lipka, *Zeitschrift für Naturforschung B*, 1983, **38**, 1615–1621. https://doi.org/10.1515/znb-1983-1213.