



Solid-State Photoinitiated Cycloaddition Reaction of 4,4'-(Ethene-1,2-diyl)bis(pyridinium) Dinitrate: Charge-Density Perspective on Initial Stage of the Reaction

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Atom	U 11	U_{22}	U 33	U 23	U 13	U 12
O(1)	19.67(17)	26.3(2)	8.20(13)	2.14(12)	-1.04(11)	4.40(15)
O(2)	10.07(12)	21.23(16)	7.80(11)	1.02(10)	0.51(9)	3.54(11)
O(3)	12.78(14)	21.17(18)	16.66(15)	0.60(13)	1.76(12)	6.47(12)
N(1)	11.34(9)	13.17(10)	8.84(9)	0.82(7)	4.10(7)	0.42(7)
N(2)	9.49(9)	12.11(10)	7.79(9)	0.91(7)	0.20(6)	0.78(7)
C(1)	8.90(10)	13.46(12)	10.30(10)	0.86(8)	3.30(7)	-1.25(8)
C(2)	8.80(10)	12.18(11)	8.34(10)	-0.08(7)	2.03(7)	-2.19(7)
C(3)	8.08(9)	8.82(10)	7.09(9)	0.16(6)	1.86(6)	-0.94(7)
C(4)	10.53(10)	12.75(11)	7.63(9)	-0.39(7)	1.17(7)	-2.39(7)
C(5)	13.51(11)	14.47(12)	7.16(10)	-0.56(8)	2.16(8)	-1.13(9)
C(6)	8.65(9)	10.98(11)	7.85(9)	0.27(7)	2.05(7)	-1.81(7)
H(1)	12.358	21.139	7.871	0.006	4.199	-5.026
H(1A)	8.031	19.842	14.581	-1.225	0.396	-7.077
H(2)	14.616	21.019	6.486	-3.052	-2.174	-4.227
H(4)	8.077	19.838	14.497	-1.425	0.077	-7.061
H(5)	14.935	20.945	6.284	-3.182	-1.838	-4.18
H(6)	13.022	13.941	6.986	-2.592	-2.752	-1.236

Table S1. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+...]$.

Table S2. Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O(1) ¹	N(2) ¹	1.2481(5)	C(2) ¹	C(3) ¹	1.4039(4)
O(2) ¹	N(2) ¹	1.2636(4)	C(3) ¹	$C(4)^{1}$	1.4051(4)
O(3) ¹	N(2) ¹	1.2497(5)	C(3) ¹	C(6) ¹	1.4629(3)
$N(1)^{1}$	$C(1)^{1}$	1.3421(4)	C(4) ¹	C(5) ¹	1.3795(4)
$N(1)^{1}$	C(5) ¹	1.3482(4)	C(6) ¹	C(6) ²	1.3477(5)
C(1) ¹	C(2) ¹	1.3846(4)			

¹+ X, +Y, +Z; ²1 - X, -Y, 1 - Z

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(1) ¹	N(1) ¹	C(5) ¹	122.19(2)	C(2) ¹	C(3) ¹	C(4) ¹	118.25(2)
O(1) ¹	N(2) ¹	O(2) ¹	119.26(4)	C(2) ¹	C(3) ¹	C(6) ¹	118.88(2)
O(1) ¹	N(2) ¹	O(3) ¹	121.06(4)	C(4) ¹	C(3) ¹	C(6) ¹	122.87(2)
O(2) ¹	N(2) ¹	O(3) ¹	119.68(3)	C(3) ¹	C(4) ¹	C(5)1	119.23(3)
N(1) ¹	$C(1)^{1}$	C(2) ¹	119.52(3)	$N(1)^{1}$	C(5) ¹	C(4) ¹	120.59(3)
C(1) ¹	C(2) ¹	C(3) ¹	120.20(3)	C(3) ¹	C(6) ¹	C(6) ²	123.83(3)
¹ +X,+Y,+Z; ² 1–X,-Y,1–Z							

Table S3. Bond Angles for 1.

Table S4. Topological properties at the bcps in 1 [atomic units].

Bond	rho	d2rho	G(r)	H(r)	V(r)
O(1)-N(2)	0.557	-0.473	1.004	-1.122	-2.125
O(2)-N(2)	0.476	-0.271	0.787	-0.854	-1.641
O(3)-N(2)	0.491	-0.316	0.826	-0.905	-1.731
N(1)-C(1)	0.356	-0.864	0.369	-0.585	-0.955
N(1)-C(5)	0.351	-1.048	0.327	-0.589	-0.915
C(1)-C(2)	0.335	-0.652	0.356	-0.519	-0.875
C(2)-C(3)	0.326	-0.724	0.323	-0.504	-0.826
C(3)-C(4)	0.310	-0.649	0.300	-0.462	-0.761
C(3)-C(6)	0.276	-0.632	0.230	-0.388	-0.618
C(4)-C(5)	0.326	-0.641	0.337	-0.497	-0.833
C(6)-X3_C(6)	0.352	-0.815	0.368	-0.572	-0.940

Residual density analysis

The residual density analysis was carried out as it was described by Henn & Meindl [*Acta Cryst. Sect. A* **2014**, *70*, 499–513.]. The test for IAM models was performed for **1** and **2** to ensure that the residual density forms a Gaussian distribution (Figure S1) allowing to attribute residual density peaks ($\Delta Q_{max}/\Delta Q_{min} = 0.77/- 0.25e Å^{-3}$) to experimental 'noise'. For the multipole refinement model of **1** the parabolic curve in the fractal diagram (Figure S2) characterized by d^f(0) = 2.74 and featureless residual density map (Figure S3) suggest a successful refinement. Normal probability plot plotted against full dataset and time scale factor plot vs. the resolution confirms good data quality over the whole resolution range and its internal consistency (Figure S4) of **1**.





Figure S1. Histogram showing residual density for IAM refinement of (a) 1 and (b) 2.

Figure S2. Plot of the fractal dimension d^f vs. the residual electron density (Q0) in the unit cell of **1**. No resolution cutoff was applied to the data used for the Fourier transformation.



Figure S3. The residual density maps in the section of (a) O(1), O(2) and O(3) atoms calculated using all data for **1**. Isocontours are drawn every 0.1 eÅ⁻³; positive contours are shown in red, the negative contours are dashed blue.



Figure S4. (a) Normal probability plot plotted against full dataset of **1**; (b) Scale factor plot against resolution; (c) $|F_0| / |F_c|$ against resolution.

Voronoi tessellation

The Voronoi polyhedron of an A atom surrounded by {Yi} atoms consists of all points that are closer to the inner atom than to any external one, and a molecule is constructed of the atomic Voronoi domains. Within ToposPro program package [V.A. Blatov, D.M. Proserpio, A.P. Shevchenko *Cryst. Growth & Des.* **2014** *14*, 3576-3586] the following descriptors of a molecular Voronoi polyhedron can be calculated: its' volume, molecular surface (and contribution of different interaction types to a total molecular surface), the second moment of inertia, and others. For each A-Y and A...Y interaction, interatomic distance, an area and solid angle of a common atomic surface, rank (**RC**) and some other characteristics can be calculated. The rank is the number of chemical bonds in the shortest chain connecting the A_i and Y_j atoms in the crystal structure. Thus, all pair interactions can automatically be divided on valence bonds (RC = 1), intramolecular non-bonded interactions (RC > 1) and intermolecular non-bonded interactions (RC = 0). The surface of molecular VDP is faceted by the faces with RC = 0 (Figure S5) and the number of intermolecular interactions ($^{\circ}$ k) is calculated as the number of these faces. Within this approach no bonding is possible between atoms that do not share any atomic surface. Minor faces of the Voronoi polyhedron (i) where the midpoint between an atomic pair lies outside their common surface and (ii) very small faces are associated with non-bonded interactions. Major faces correspond to valence bonds and directional intermolecular interactions.



Figure S5. Molecular Voronoi polyhedron of H₂bpe²⁺ cation in 1.

Powder X-Ray Diffraction

Powder patterns (Figure S6) were measured on a Bruker D8 Advance diffractometer with motorized slits and Ni filter at room temperature with CuK α radiation (λ = 1.54060 Å), $\theta/2\theta$ scan from 4 to 60° in reflection mode. The powder patterns were modelled with the Rietveld method using Bruker TOPAS5 [Topas4.2 User Manual. BrukerAXS GmbH, 2009] software. The fundamental parameters approach [R. W. Cheary, A. Coelho *J. Appl. Crystallogr.* **1992** *25*, 109–121.] was used for the profile fitting. The preferred orientation was taken into account with the spherical harmonics approach [M. Jarvinen J. Appl. Crystallogr. **1993** *26*, 525–531.]. During refinement, the background, profile, preferred orientation, and unit cell parameters were refined.





Figure S6. Powder XRD patterns of bulk sample **1** (a) before and (b) after irradiation. Rietveld analysis indicates presence that the sample consists mainly from phase **1** and **2**. The blue line is the experimental pattern, the fuchsia line is the calculated pattern, and the grey line is the difference curve. R_{wp}/R_{bragg} for (a) and (b) are equal to 9.591/1.347 and 4.335/0.343.

¹H NMR data



Figure S7. ¹H NMR spectrum of 2.