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Directional growth, physicochemical and quantum chemical investigations on Pyridinium 2-carboxylate: 4-nitrophenol (P2C4N) single crystal for nonlinear optical (NLO) applications

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SUPPLEMENTARY INFORMATION

1. Determination of linear optical parameters

The absorption coefficient of the grown crystal was evaluated using optical transmission data by the following equation

$$\alpha = \frac{2.303 \times \log\left(\frac{1}{T}\right)}{t} \quad \text{----------(1)}$$

where 'T' is the percentage of transmittance and 't' is the thickness of the sample (1 mm) which was used in UV-Vis-NIR transmittance analysis. Optical band gap (E_g) was evaluated using Tauc's plot relation by the following equation [1]

$$\alpha h\upsilon = A(h\upsilon - E_g)^n \quad \text{----------(2)}$$

where 'E_g'denotes the band gap of the sample, 'A' is a constant, 'h' is Planck's constant, 'υ' is the frequency of the incident photon and 'n' is the characteristics of an electronic transition of the given material. In the above relation, if n=1/2 for direct allowed transitions, n=3/2 for direct forbidden transitions, n=2 for indirect allowed transitions and n=3 for indirect forbidden transitions [2].

The reflectance (R) in terms of absorption coefficient can be calculated by the following equation

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)\,T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)\,T} \text{------} (2)$$

The refractive index (n_0) of the grown crystal was determined by the following equation [3]

$$n_0 = -(R+1) \pm 2\frac{\sqrt{R}}{(R-1)} \text{----------} (3)$$

The extinction coefficient of the title crystal was determined by the following equation

$$K = \frac{\lambda\alpha}{4\pi} \text{----------} (4)$$

2. Determination of third-order nonlinear optical (NLO) parameters

The Rayleigh diffraction length (Z_R) of laser beam was calculated by the following equation [4]

$$Z_R = \frac{K\omega_0{}^2}{2} \text{----------} (5)$$

where, 'K' denotes the wavevector ($K=2\pi/\lambda$) and 'ω_0' is the beam waist at the focal point. The beam waist (ω_0) of the laser source can be calculated by the following equation [4]

$$\omega_0 = \frac{f\lambda}{D} \text{----------} (6)$$

where, 'f' denotes the focal length of the lens, 'λ' is the wavelength of the source and 'D' is the beam radius at the lens. In order to determine the nonlinear refractive index (n_2), the difference between normalized peak and valley transmittance (ΔTp–v) from the closed aperture (Fig.13b) can be calculated in terms of axis phase shift ($|\Delta\phi|$) at the focus by the following equation [5]

$$|\Delta\phi| = \frac{\Delta T_{P-V}}{0.406\,(1-S)^{0.25}} \text{----------} (7)$$

where, 'S' is the linear transmittance of the aperture and it is calculated using the following relation

$$S = 1 - \exp\left(\frac{-2r_a^2}{\omega_a^2}\right) \text{----------} (8)$$

where 'r_a'denotes the radius of the aperture and 'w_a' denotes the beam radius at the aperture. The third-order nonlinear refractive index (n_2) of the grown crystal was determined by the following relation

$$n_2 = \frac{\Delta\Phi_0}{KI_0L_{eff}} \text{----------} (9)$$

where, $K = \frac{2\pi}{\lambda}$, 'L_{eff}' is the effective thickness of the sample and 'I_0' is the intensity of the laser beam at the focal point. The effective thickness 'L_{eff}' can be calculated by the following relation

$$L_{eff} = \frac{[1 - \exp(-\alpha L)]}{\alpha} \text{----------} (10)$$

where 'α' is the linear absorption coefficient and it was obtained by UV-Vis-NIR transmittance analysis and 'L' denotes the thickness of the crystal which is used for the UV-Vis-NIR analysis. From OP curve (Fig. 13a), the nonlinear refractive index of absorption coefficient (β) can be calculated using the following relation [4]

$$\beta = \frac{2\sqrt{2}\,\Delta T}{I_0L_{eff}} \text{----------} (11)$$

where 'ΔT' is normalized peak transmittance in the open aperture curve (Z=0). Based on the results, the real and imaginary parts of the third-order nonlinear optical susceptibility can be calculated by the following relations [6]

$$\text{Re}\,\chi^{(3)}\,(\text{esu}) = \frac{10^{-4}\,(\varepsilon_0 C^2 n_0^2 n_2)}{\pi}\left(\frac{cm^2}{W}\right) \text{---------(12)}$$

$$\text{Im}\,\chi^{(3)}\,(\text{esu}) = \frac{10^{-2}\,(\varepsilon_0 C^2 n_0 \lambda\beta)}{4\pi^2}\left(\frac{cm}{W}\right) \text{----------(13)}$$

where, 'ε_o' denotes the vacuum permittivity (8.851×10^{-12} F/m), 'C' denotes the velocity of light in vacuum (3×10^8 m/s) and 'n_0' denotes the linear refractive index of P2C4N crystal. The n_0 was calculated from UV-Vis-NIR analysis at 632 nm and it was found to be 1.35. The absolute third-order nonlinear susceptibility of the title crystal can be calculated by the following relation.

$$\left|\chi^{(3)}\right| = [(\text{Re}(\chi^{(3)}))^2 + (\text{Im}(\chi^{(3)}))^2]^{1/2}\ \text{esu} \text{---------(14)}$$

Further, the second-order hyperpolarizability (γ) of the title crystal was estimated by the following equation [6]

$$\text{Re}\,[\gamma] = \frac{\text{Re}\,(\chi^{(3)})}{Nf^4} \text{--------------------(15)}$$

where, 'N' is the number of molecules per unit volume and it can be obtained by the following equation

$$N = \frac{\rho^*\,(N_A)}{M} \text{--------------------(16)}$$

where '(ρ^*)' denotes the density of P2C4N crystal, 'N_A' denotes the Avogadro number and 'M' denotes the molecular weight. The local field correction factor (f) can be obtained from the following equation

$$f = \frac{(n_0^2 + 2)}{3} \text{--------------------(17)}$$

where, 'n_o' denotes the linear refractive index of the grown crystal and it was calculated by the UV-Vis-NIR analysis. The coupling factor can be determined by the ratio of the imaginary and real part of the third-order susceptibility of the grown crystal [7]

$$\rho^* = \mathrm{Im}\,(\chi^{(3)}) / \mathrm{Re}\,(\chi^{(3)}) \text{ ----------(18)}$$

In order to know the suitability of the grown crystal for optical switching applications, two figure of merit were evaluated using the following equations [8]

$$W = n_2 I_0 / \alpha\lambda \text{ ----------(19)}$$

$$T = \beta\lambda / n_2 \text{ ----------(20)}$$

where, 'n_2' is nonlinear refractive index, 'I_0' is the intensity of the laser beam (I_0=26.31 MW/m^2), 'α' is linear absorption coefficient, 'λ' is wavelength of laser source and 'β' is nonlinear absorption coefficient.

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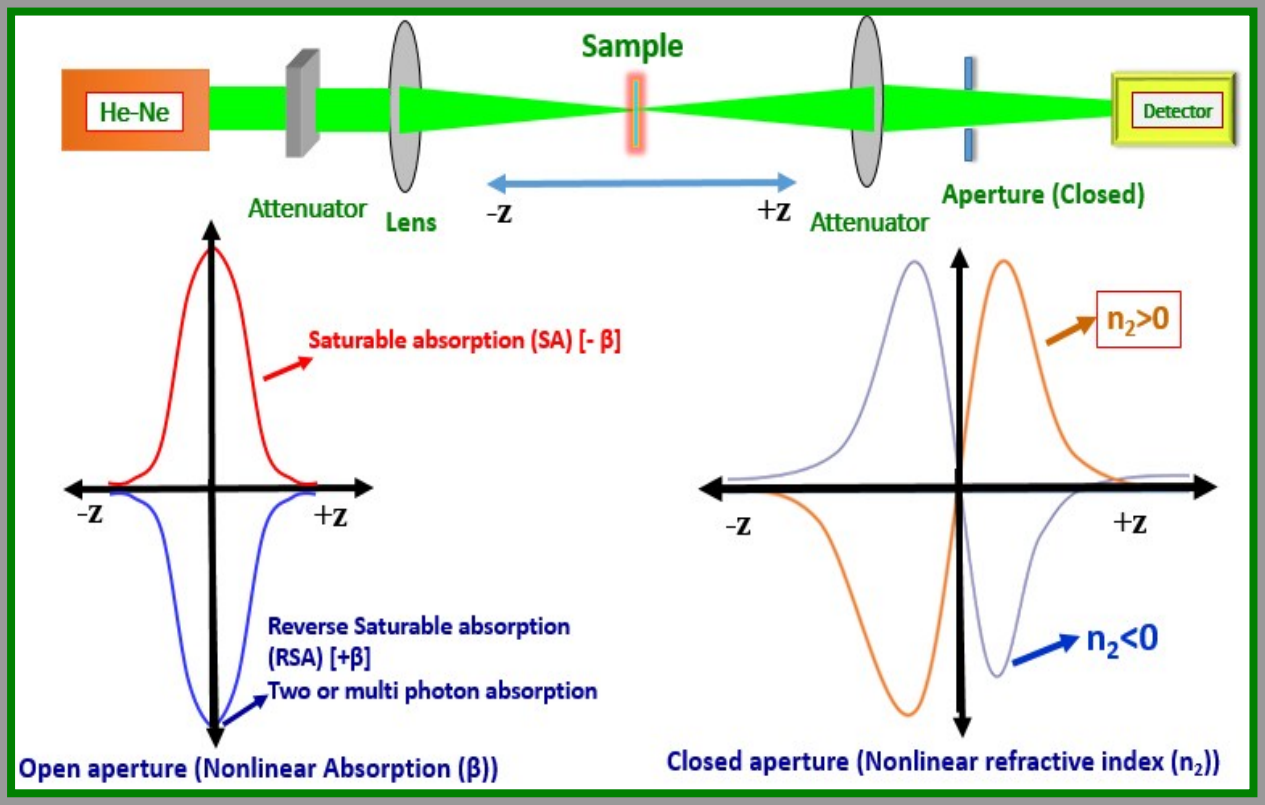

Fig.S1. Z-scan experimental setup

S. No	Temperature at top portion (°C)	Temperature at bottom portion (°C)	Growth observations (Solvent-Methanol)	Growth rate
1	**37**	**34**	Multi-nucleation was formed at top of the glass ampoule	Crystal growth is not possible
2	**36**	**34**	Poor quality crystal	Growth rate is above ~3 mm/day
3	**35**	**35**	(Multi nucleation was effectively controlled) Good quality crystals	Optimized growth rate is ~3 mm/day (Growth period is 60 days)

Table.S1. Growth observation of unidirectional SR method grown P2C4N crystal

Bond length(Å)	XRD	B3LYP/ cc-pVTZ	Bond angle (^{0})	XRD	B3LYP/ cc-pVTZ	Dihedral angle (^{0})	XRD	B3LYP/ cc-pVTZ
C_1-C_8	1.3673	1.3838	C_8-C_1-C_{10}	124.8498	128.3031	C_{10}-C_1-C_8-C_6	179.957	-180.01
C_1-C_{10}	1.5155	1.5441	C_8-C_1-N_{11}	118.3769	118.9879	C_{10}-C_1-C_8-H_9	-0.0295	-0.0092
C_1-N_{11}	1.3350	1.3388	C_{10}-C_1-N_{11}	116.7710	112.709	N_{11}-C_1-C_8-C_6	0.5140	-0.0028
C_2-H_3	0.9299	1.0792	H_3-C_2-C_4	120.1254	123.962	N_{11}-C_1-C_8-H_9	-179.472	179.9975
C_2-C_4	1.3625	1.3778	H_3-C_2-N_{11}	120.0949	117.3405	C_8-C_1-C_{10}-O_{12}	178.590	180.0131
C_2-N_{11}	1.3350	1.3401	C_4-C_2-N_{11}	119.7796	118.6975	C_8-C_1-C_{10}-O_{13}	-2.9456	0.015
C_4-H_5	0.9295	1.0792	C_2-C_4-H_5	120.4433	119.6798	N_{11}-C_1-C_{10}-O_{12}	-1.9580	0.0068
C_4-C_6	1.3635	1.397	C_2-C_4-C_6	119.0821	119.0252	N_{11}-C_1-C_{10}-O_{13}	176.505	180.0086
C_6-H_7	0.9302	1.0816	H_5-C_4-C_6	120.4744	121.295	C_8-C_1-N_{11}-C_2	-0.5953	0.0015
C_6-C_8	1.3800	1.3877	C_4-C_6-H_7	120.0556	119.5774	C_8-C_1-N_{11}-H_{14}	-0.5953	-180.003
C_8-H_9	0.9305	1.0795	C_4-C_6-C_8	119.8945	120.3121	C_{10}-C_1-N_{11}-C_2	179.916	180.0072
C_{10}-O_{12}	1.2329	1.2441	H_7-C_6-C_8	120.0497	120.1105	C_{10}-C_1-N_{11}-H_{14}	3.4454	0.0031
C_{10}-O_{13}	1.2352	1.2404	C_1-C_8-C_6	119.8384	118.7051	H_3-C_2-C_4-H_5	0.7226	-0.0021
N_{11}-H_{14}	0.8669	1.0352	C_1-C_8-H_9	120.0951	118.2175	H_3-C_2-C_4-C_6	-179.298	-180.003
O_{13}-H_{29}	1.7732	1.7189	C_6-C_8-H_9	120.0664	123.0774	N_{11}-C_2-C_4-H_5	-179.267	-180.001
C_{15}-C_{16}	1.3934	1.4041	C_1-C_{10}-O_{12}	116.6164	112.2723	N_{11}-C_2-C_4-C_6	0.7108	-0.0018

C_{15}-C_{23}	1.3904	1.4043	C_1-C_{10}-O_{13}	115.8770	114.7467	H_3-C_2-N_{11}-C_1	179.989	180.0017
C_{15}-O_{26}	1.3362	1.3369	O_{12}-C_{10}-O_{13}	127.4855	132.981	H_3-C_2-N_{11}-H_{14}	-3.5025	0.0064
C_{16}-H_{17}	0.9299	1.0808	C_1-N_{11}-C_2	123.0216	124.2722	C_4-C_2-N_{11}-C_1	-0.0203	0.0009
C_{16}-C_{18}	1.3678	1.379	C_1-N_{11}-H_{14}	119.0020	109.6662	C_4-C_2-N_{11}-H_{14}	176.487	180.0056
C_{18}-H_{19}	0.9299	1.0788	C_2-N_{11}-H_{14}	117.8861	126.0616	C_2-C_4-C_6-H_7	179.2051	179.9987
C_{18}-C_{20}	1.3794	1.3929	C_{10}-O_{13}-H_{29}	117.8950	127.3267	C_2-C_4-C_6-C_8	-0.7725	0.0004
C_{20}-C_{21}	1.3812	1.3915	C_{16}-C_{15}-C_{23}	119.2379	119.4638	H_5-C_4-C_6-H_7	-0.8163	-0.0019
C_{20}-N_{25}	1.4482	1.4568	C_{16}-C_{15}-O_{26}	117.5051	117.4851	H_5-C_4-C_6-C_8	179.206	179.9998
C_{21}-H_{22}	0.9298	1.0789	C_{23}-C_{15}-O_{26}	123.2501	123.0511	C_4-C_6-C_8-C_1	0.1616	0.0019
C_{21}-C_{23}	1.3705	1.3817	C_{15}-C_{16}-H_{17}	119.7136	118.5331	C_4-C_6-C_8-H_9	-179.851	-179.998
C_{23}-H_{24}	0.9295	1.0818	C_{15}-C_{16}-C_{18}	120.5756	120.4723	H_7-C_6-C_8-C_1	-179.815	180.0036
N_{25}-O_{27}	1.2223	1.2275	H_{17}-C_{16}-C_{18}	119.7106	120.9946	H_7-C_6-C_8-H_9	0.1707	0.0033
N_{25}-O_{28}	1.2250	1.2276	C_{16}-C_{18}-H_{19}	120.3380	121.3076	C_1-C_{10}-O_{13}-H_{29}	171.736	180.0116
O_{26}-H_{29}	0.8384	0.9881	C_{16}-C_{18}-C_{20}	119.2414	119.399	O_{12}-C_{10}-O_{13}-H_{29}	-9.9948	0.0139
			H_{19}-C_{18}-C_{20}	120.4205	119.2934	C_{10}-O_{13}-O_{26}-C_{15}	65.2125	0.0093
			C_{18}-C_{20}-C_{21}	121.1985	120.8909	C_{23}-C_{15}-C_{16}-H_{17}	-178.446	-180.004
			C_{18}-C_{20}-N_{25}	119.6131	119.5235	C_{23}-C_{15}-C_{16}-C_{18}	1.6343	-0.0049
			C_{21}-C_{20}-N_{25}	119.1859	119.5856	O_{26}-C_{15}-C_{16}-H_{17}	2.4709	-0.003
			C_{20}-C_{21}-H_{22}	120.2803	119.2221	O_{26}-C_{15}-C_{16}-C_{18}	-177.448	179.9961
			C_{20}-C_{21}-C_{23}	119.4079	119.8506	C_{16}-C_{15}-C_{23}-C_{21}	-2.1391	0.0038
			H_{22}-C_{21}-C_{23}	120.3117	120.9273	C_{16}-C_{15}-C_{23}-H_{24}	177.878	179.9999
			C_{15}-C_{23}-C_{21}	120.3083	119.9235	O_{26}-C_{15}-C_{23}-C_{21}	176.888	-179.997
			C_{15}-C_{23}-H_{24}	119.8527	119.7967	O_{26}-C_{15}-C_{23}-H_{24}	-3.0941	-0.0011
			C_{21}-C_{23}-H_{24}	119.8389	120.2798	C_{16}-C_{15}-O_{26}-H_{29}	172.6174	179.9557
			C_{20}-N_{25}-O_{27}	118.1174	118.1174	C_{23}-C_{15}-O_{26}-H_{29}	-6.4256	-0.0432
			C_{20}-N_{25}-O_{28}	118.6440	118.1429	C_{15}-C_{16}-C_{18}-H_{19}	179.445	-179.997
			O_{27}-N_{25}-O_{28}	122.8478	123.7397	C_{15}-C_{16}-C_{18}-C_{20}	-0.5329	0.0021
			C_{15}-O_{26}-H_{29}	109.4443	112.909	H_{17}-C_{16}-C_{18}-H_{19}	-0.4743	0.0018
						H_{17}-C_{16}-C_{18}-C_{20}	179.547	-179.999
						C_{16}-C_{18}-C_{20}-C_{21}	-0.0857	0.0017
						C_{16}-C_{18}-C_{20}-N_{25}	179.3357	180.0013
						H_{19}-C_{18}-C_{20}-C_{21}	179.936	180.0011
						H_{19}-C_{18}-C_{20}-N_{25}	-0.6424	0.0007
						C_{18}-C_{20}-C_{21}-H_{22}	179.590	-180
						C_{18}-C_{20}-C_{21}-C_{23}	-0.4180	-0.0028
						N_{25}-C_{20}-C_{21}-H_{22}	0.1665	0.001
						N_{25}-C_{20}-C_{21}-C_{23}	-179.841	179.9977
						C_{18}-C_{20}-N_{25}-O_{27}	-1.3651	0.0238
						C_{18}-C_{20}-N_{25}-O_{28}	178.095	-179.975

						C_{21}-C_{20}-N_{25}-O_{27}	178.068	-179.977
						C_{21}-C_{20}-N_{25}-O_{28}	-2.4711	0.0248
						C_{20}-C_{21}-C_{23}-C_{15}	1.5379	-0.0001
						C_{20}-C_{21}-C_{23}-H_{24}	-178.479	-179.996
						H_{22}-C_{21}-C_{23}-C_{15}	-178.470	-180.003
						H_{22}-C_{21}-C_{23}-H_{24}	1.5117	0.0005

Table.S2. The comparison of bond lengths, bond angles, dihedral angle for P2C4N by the single crystal XRD and DFT method

Donor(j)	Acceptor		$E^{(2)}$ (kcal/mol)	E(j)-E(j)	F(i,j)
σ (C_1 - C_8)	σ *(C_1 – C_{10})	1.96906	0.96	1.09	0.03
σ (C_1 - C_8)	σ *(C_1 - N_{11})		0.79	1.2	0.028
σ (C_1 - C_8)	σ *(C_6 - H_7)		2.7	1.14	0.05
σ (C_1 - C_8)	σ *(C_6 - C_8)		1.59	1.26	0.04
σ (C_1 - C_8)	σ *(C_8 - H_9)		0.88	1.16	0.029
σ (C_1 - C_8)	σ *(N_{11} - H_{14})		2.54	1.1	0.048
σ (C_1 - C_{10})	σ *(C_1 - C_8)		1.18	1.12	0.033
σ (C_1 - C_{10})	σ *(C_1 - C_{10})	1.96906	0.82	0.95	0.026
σ (C_1 - C_{10})	σ *(C_2 - N_{11})		6.39	1.04	0.073
σ (C1 - C10)	σ *(C6 - C8)		2.9	1.12	0.051
σ (C1 - C10)	σ *(N11 - H14)		0.98	0.96	0.028
σ (C1 - N11)	σ *(C1 - C8)		1.21	1.4	0.037
σ (C1 - N11)	σ *(C2 - H3)		1.71	1.25	0.041
σ (C1 - N11)	σ *(C2 - N11)		1.58	1.32	0.041
σ (C1 - N11)	σ *(C8 - H9)		1.68	1.3	0.042
σ (C1 - N11)	σ *(C10 - O13)		0.75	1.49	0.03
σ (C1 - N11)	σ *(N11 - H14)		0.7	1.24	0.026
σ (C1 - N11)	π *(C1 - N11)		0.52	0.33	0.013
σ (C1 - N11)	π *(C2 - C4)		22.94	0.36	0.083
σ (C1 - N11)	π *(C10 - O13)		5.36	0.42	0.045
σ (C2 - H3)	σ *(C1 - N11)		6.21	1.03	0.072
σ (C2 - H3)	σ *(C 2 - C4)		0.64	1.08	0.023
σ (C2 - H3)	σ *(C4 - C6)		3.7	1.07	0.056
σ (C2 - H3)	σ *(N11 - H14)		0.51	0.93	0.02
σ (C2 - C4)	σ *(C2 - H3)		0.96	1.13	0.029
σ (C2 - C4)	σ *(C2 - N11)		0.87	1.2	0.029
σ(C2 - C4)	σ *(C4 - H5)		0.72	1.16	0.026
σ (C2 - C4)	σ *(C4 - C6)		1.45	1.25	0.038

σ (C2 - C4)	σ *(C6 - H7)		2.43	1.16	0.048
σ (C2 - C4)	σ *(N11 - H14)		3.35	1.12	0.055
π (C2 - C4)	π *(C1 - N11)		13.45	0.25	0.054
π (C2 - C4)	π *(C2 - C4)		0.97	0.29	0.015
σ (C2 - N11)	σ *(C1 - C10)		1.6	1.25	0.041
σ (C2 - N11)	σ *(C1 - N11)		1.84	1.35	0.045
σ (C2 - N11)	σ *(C 2 - C4)		1.1	1.4	0.035
σ (C2 - N11)	σ *(C4 - H5)		1.62	1.3	0.041
σ (C2 - N11)	σ *(N11 - H14)		0.57	1.26	0.024
σ (C4 - H5)	σ *(C2 - N11)		4.83	0.99	0.062
σ (C4 - H5)	σ *(C6 - C8)		4.13	1.07	0.059
σ (C4 - C6)	σ *(C2 - H3)		2.81	1.11	0.05
σ (C4 - C6)	σ *(C2 - C4)		1.45	1.24	0.038
σ (C4 - C6)	σ *(C4 - H5)		0.89	1.14	0.028
σ (C4 - C6)	σ *(C 6 - H 7)		0.59	1.14	0.023
σ (C4 - C6)	σ *(C6 - C8)		1.45	1.26	0.038
σ (C4 - C6)	σ *(C8 - H9)		2.65	1.16	0.05
σ (C6 - H7)	σ *(C1 - C8)		4.46	1.07	0.062
σ (C6 - H7)	σ *(C2 - C4)		4.43	1.05	0.061
σ (C6 - H7)	σ *(C4 - H5)		0.52	0.95	0.02
σ (C6 - C8)	σ *(C1 - C8)		1.56	1.26	0.04
σ (C6 - C8)	σ *(C1 - C10)		3.56	1.09	0.057
σ (C6 - C8)	σ *(C4 - H5)		2.58	1.14	0.048
σ (C6 - C8)	σ *(C4 - C6)		1.45	1.23	0.038
σ (C6 - C8)	σ *(C6 - H7)		0.69	1.14	0.025
σ (C6 - C8)	σ *(C8 - H9)		0.93	1.16	0.029
σ (C8 - H9)	σ *(C1 - C8)		0.7	1.05	0.024
σ (C8 - H9)	σ *(C1 - N11)		6	0.99	0.069
σ (C8 - H9)	σ *(C4 - C6)		4.37	1.03	0.06
σ (C8 - H9)	σ *(C6 - H7)		0.54	0.93	0.02
σ (C10 - O12)	σ *(C1 - C8)		1.68	1.49	0.045
σ (C10 - O12)	σ *(C 10 - O13)		1.96	1.58	0.05
σ (C10 - O13)	σ *(C1 - N11)		1.12	1.43	0.036
σ (C10 - O13)	σ *(C10 - O12)		2.14	1.57	0.052
σ (C10 - O13)	π *(C1 - N11		6.39	0.27	0.042
σ (C10 - O13)	π *(C10 - O13		1.74	0.36	0.025
σ (N11 - H14)	σ *(C1 - C8)		4.92	1.2	0.069
σ (N11 - H14)	σ *(C1 - C10)		0.55	1.03	0.022
σ N 11 - H 14	σ *(C1 - N11)		0.73	1.14	0.026
σ N 11 - H 14	σ *(C2 - H3)		0.88	1.05	0.027
σ N 11 - H 14	σ *(C2 - C4)		3.05	1.19	0.054
n_1C 8	π *(C1 - N11)		160.26	0.09	0.126
n_1C 8	π *(C10 - O13)		0.56	0.17	0.011
n_1O 12	σ *(C1 - C10)		2.79	1.03	0.049

n_1O 12	σ *(C10 - O13)		2.67	1.29	0.053
n_1O 12	σ *(N11 - H14)		1.24	1.04	0.032
LP (2) O 12	σ *(C1 - C8)		0.95	0.74	0.025
LP (2) O 12	σ *(C1 - C10)		21.77	0.58	0.1
LP (2) O 12	σ *(C2 - N11)		0.8	0.66	0.021
LP (2) O 12	σ *(C10 - O13)		19.78	0.83	0.118
LP (2) O 12	σ *(N11 - H14)		6.26	0.58	0.055
LP (3) O 12	π *(C10 - O13)		120.36	0.25	0.154
n_1O 13	σ *(C1 - C10		0.55	1.01	0.022
n_1O 13	σ *(C10 - O12)		6.9	1.26	0.084
LP (2) O 13	σ *(C1 - C10)		25.28	0.59	0.109
LP (2) O 13	σ *(C1 - N11)		1.14	0.7	0.026
LP (2) O 13	σ *(C10 - O12)		14.29	0.84	0.1
π *(C1 - N11)	π *(C2 - C4)		69.45	0.03	0.069
π *(C1 - N11)	π *(C10 - O13)		35.4	0.09	0.074
σ(C1 - C10)	σ *(C23 - H24)		0.09	1.11	0.009
σ (C1 - C10)	σ *(O26 - H29)		0.32	1.09	0.017
n_1O 12	σ *(C23 - H24)		0.35	1.19	0.018
LP (2) O 12	σ *(C23 - H24)		1.1	0.73	0.026
n_1O 13	σ *(C15 - O26)		0.11	1.12	0.01
n_1O 13	σ *(O26 - H29)		6.46	1.14	0.077
LP (2) O 13	σ *(C15 - O26)		0.1	0.7	0.008
LP (2) O 13	σ *(O26 - H29)		15.25	0.73	0.096
LP (2) O 26	π *(C10 - O13)		0.05	0.28	0.004
σ(C15 - C16)	σ *(C15 - C23)		2.14	1.22	0.046
σ(C15 - C16)	σ *(C16 - H17)		0.68	1.11	0.025
σ(C15 - C16)	σ *(C16 - C18)		1.9	1.25	0.044
σ (C15 - C16	σ *(C18 - H19)		2.71	1.13	0.049
σ (C15 - C16)	σ *(C23 - H24)		2.4	1.14	0.047
σ (C15 - C16)	σ *(O26 - H29)		2.29	1.12	0.045
σ (C15 - C23)	σ *(C15 - C16)		2.32	1.22	0.048
σ (C15 - C23)	σ *(C16 - H17)		2.29	1.12	0.045
σ (C15 - C23)	σ *(C21 - H22)		2.66	1.13	0.049
σ (C15 - C23)	σ *(C21 - C23)		2.03	1.26	0.045
σ (C15 - C23)	σ *(C23 - H24)		0.81	1.14	0.027
σ (C15 - O26)	σ *(C15 - C16		0.6	1.44	0.026
σ (C15 - O26	σ *(C15 - C23)		0.78	1.45	0.03
σ (C15 - O26)	σ *(C16 - C18)		1.57	1.48	0.043
σ (C15 - O26)	σ *(C21 - C23)		1.31	1.48	0.039
σ (C16 - H17)	σ *(C15 - C23)		4.3	1.04	0.06
σ (C16 - H17)	σ *(C15 - O26)		0.75	0.91	0.023
σ (C16 - H17)	σ *(C16 - C18)		0.63	1.08	0.023
σ (C16 - H17)	σ *(C18 - C20)		4.5	1.05	0.061
σ (C16 - C18)	σ *(C15 - C16)		1.46	1.23	0.038

σ (C16 - C18)	σ *(C15 - O26)		3.42	1.11	0.055
σ (C16 - C18)	σ *(C16 - H17)		0.98	1.13	0.03
σ (C16 - C18)	σ *(C18 - H19)		0.92	1.15	0.029
σ (C16 - C18)	σ *(C18 - C20)		2.12	1.24	0.046
σ (C16 - C18)	σ *(C20 - N25)		4.62	1	0.062
σ (C18 - H19)	σ *(C15 - C16)		4.57	1.04	0.061
σ (C18 - H19)	σ *(C16 - H17)		0.52	0.94	0.02
σ (C18 - H19)	σ *(C16 - C18)		0.65	1.08	0.024
σ (C18 - H19)	σ *(C20 - C21)		4.96	1.05	0.065
σ (C18 - H19)	σ *(C20 - N25)		0.66	0.81	0.021
σ (C18 - C20)	σ *(C16 - H17)		2.84	1.13	0.051
σ (C18 - C20)	σ *(C16 - C18)		1.83	1.27	0.043
σ (C18 - C20)	σ *(C18 - H19)		0.9	1.14	0.029
σ (C18 - C20)	σ *(C20 - C21)		3.7	1.24	0.06
σ (C18 - C20)	σ *(C21 - H22)		2.33	1.14	0.046
σ (C18 - C20)	σ *(N25 - O28)		2.46	1.13	0.047
σ (C20 - C21)	σ *(C18 - H19)		2.35	1.14	0.046
σ (C20 - C21)	σ *(C18 - C20)		3.68	1.24	0.06
σ(C20 - C21)	σ *(C21 - H22)		0.89	1.14	0.028
σ (C20 - C21)	σ *(C21 - C23)		1.78	1.27	0.043
σ (C20 - C21)	σ *(C23 - H24)		2.68	1.15	0.05
σ (C20 - C21)	σ *(N25 - O27)		2.44	1.13	0.047
σ (C20 - N25)	σ *(C16 - C18)		1.73	1.35	0.043
σ (C20 - N25)	σ *(C18 - C20)		0.61	1.33	0.025
σ (C20 - N25)	σ *(C20 - C21)		0.63	1.33	0.026
σ (C20 - N25)	σ *(C21 - C23)		1.76	1.35	0.044
σ (C21 - H22)	σ *(C15 - C23)		4.65	1.04	0.062
σ (C21 - H22)	σ *(C18 - C20)		5.02	1.05	0.065
σ (C21 - H22)	σ *(C20 - N25)		0.68	0.81	0.021
σ (C21 - H22)	σ *(C21 - C23		0.64	1.08	0.024
σ (C21 - H22)	σ *(C23 - H24)		0.53	0.96	0.02
σ (C21 - C23)	σ *(C15 - C23)		1.55	1.23	0.039
σ (C21 - C23)	σ *(C15 - O26)		4.18	1.1	0.061
σ (C21 - C23)	σ *(C20 - C21)		2.13	1.24	0.046
σ (C21 - C23)	σ *(C20 - N25)		4.63	1	0.062
σ (C21 - C23)	σ *(C21 - H22)		0.9	1.14	0.029
σ (C21 - C23)	σ *(C23 - H24)		1.08	1.15	0.032
σ (C23 - H24)	σ *(C15 - C16)		4.17	1.03	0.059
σ (C23 - H24)	σ *(C15 - O26)		0.63	0.91	0.021
σ (C23 - H24)	σ *(C20 - C21)		4.3	1.05	0.06
σ (C23 - H24)	σ *(C21 - H22)		0.51	0.95	0.02
σ (C23 - H24)	σ *(C21 - C23)		0.78	1.07	0.026
σ (N25 - O27)	σ *(C20 - C21)		1.14	1.6	0.038
σ (N25 - O27)	σ *(C20 - N25)		0.56	1.35	0.025

σ (N25 - O27)	π *(N25 - O27)		7.82	0.32	0.054
σ (N25 - O28)	σ *(C18 - C20)		1.13	1.59	0.038
σ (N25 - O28)	σ *(C20 - N25)		0.56	1.35	0.025
σ (O26 - H29)	σ *(C15 - C16)		5.33	1.26	0.073
n_1C 20	π *(C16 - C18)		64.74	0.16	0.108
n_1C 20	π *(C21 - C23)		65.27	0.16	0.108
n_1C 20	π *(N25 - O27)		757.14	0.01	0.09
n_1O 26	σ *(C15 - C16)		0.63	1.08	0.023
n_1O 26	σ *(C15 - C23)		8.85	1.09	0.088
n_1O 27	σ *(C20 - N 25)		4.77	1.07	0.065
n_1O 27	σ *(N 25 - O28)		2.68	1.21	0.051
LP (2) O 27	σ *(C16 - C18)		0.67	0.84	0.022
LP (2) O 27	σ *(C20 - C21)		0.82	0.81	0.024
LP (2) O 27	σ *(C20 - N25)		14.22	0.57	0.08
LP (2) O 27	σ *(N25 - O28)		19.33	0.7	0.105
n_1O 28	σ *(C20 - N25)		4.77	1.07	0.065
n_1O 28	σ *(25 - O27)		2.68	1.21	0.051
LP (2) O 28	σ *(C18 - C20)		0.82	0.81	0.024
LP (2) O 28	σ *(C20 - N25)		14.23	0.57	0.081
LP (2) O 28	σ *(C21 - C23)		0.67	0.84	0.022
LP (2) O 28	σ *(N25 - O27)		19.32	0.7	0.105
LP (3) O 28	π *(N25 - O27)		159.61	0.14	0.139

Table.S3. Second-order perturbation theory analysis of Fock matrix in NBO basis

RCP	Name	Atom count	ρ	$\nabla^2\rho$
1	RCP1	6	0.026021	0.167904
2	RCP2	5	0.029197	0.176551
3	RCP3	8	0.004723	0.017498
4	RCP4	6	0.024176	0.148334

Table.S4. Characteristics of the ring CPs of P2C4N

BCP	Name	Atoms	ρ	$\nabla^2\rho$	Ellipticity	K
1	BCP1	C_{10} - O_{12}	0.395982	-0.59981	0.110473	0.673827
2	BCP2	C_1 - N_{11}	0.333354	-0.76741	0.049919	0.509987
3	BCP3	C_2 - C_4	0.333136	-1.13811	0.220928	0.399496
4	BCP4	C_2 - N_{11}	0.332658	-0.79888	0.129743	0.50324
5	BCP5	C_2 - H_3	0.301899	-1.24958	0.023183	0.346448
6	BCP6	C_4 - C_6	0.320136	-1.05694	0.162463	0.365986
7	BCP7	C_4 - H_5	0.297706	-1.2081	0.01348	0.340255
8	BCP8	C_{10} - O_{13}	0.398189	-0.5929	0.122627	0.681409
9	BCP9	C_1 - C_8	0.330857	-1.12936	0.168437	0.391851
10	BCP10	C_1 - C_{10}	0.245602	-0.61602	0.101877	0.212643
11	BCP11	C_6 - H_7	0.298513	-1.21813	0.002764	0.340604
12	BCP12	C_6 - C_8	0.325906	-1.09151	0.171019	0.379915
13	BCP13	C_8 - H_9	0.299457	-1.22968	0.01171	0.342127
14	BCP14	N_{11} - H_{14}	0.326188	-1.94922	0.019127	0.53139
15	BCP15	O_{12} - H_{24}	0.0101	0.035156	0.003142	-0.00163
16	BCP16	O_{12} - H_{14}	0.033106	0.124351	0.365731	-0.00201
17	BCP17	O_{13} - H_{29}	0.043442	0.098612	0.007538	0.008438
18	BCP18	O_{26} - H_{29}	0.338109	-2.50664	0.013705	0.694787
19	BCP19	C_{15} - C_{16}	0.320025	-1.0571	0.207141	0.364347
20	BCP20	C_{16} - H_{17}	0.29373	-1.17047	0.023069	0.33437
21	BCP21	C_{16} - C_{18}	0.3284	-1.09963	0.218135	0.387859
22	BCP22	C_{15} - C_{23}	0.317952	-1.03782	0.20131	0.361363
23	BCP23	C_{18} - H_{19}	0.298217	-1.21177	0.011131	0.34122
24	BCP24	C_{18} - C_{20}	0.3221	-1.062	0.202924	0.37104
25	BCP25	C_{23} - H_{24}	0.295329	-1.18289	0.019802	0.335044

26	BCP26	C_{21} - C_{23}	0.326524	-1.08666	0.210652	0.383588
27	BCP27	C_{20} - N_{25}	0.269117	-0.73517	0.193812	0.327013
28	BCP28	N_{25} - O_{27}	0.503162	-1.11301	0.112268	0.658052
29	BCP29	C_{20} - C_{21}	0.323036	-1.06789	0.204425	0.373344
30	BCP30	N_{25} - O_{28}	0.503045	-1.11222	0.112189	0.657719
31	BCP31	C_{21} - H_{22}	0.298263	-1.21199	0.011194	0.341215
32	BCP32	C_{15} - O_{26}	0.313884	-0.59365	0.019113	0.48432

Table.S5. Characteristics of the bond CPs of P2C4N