

Electronic supplementary information (ESI)

**Single-photon ionization induced C-C or C-N bonds  
formation in pyrrole clusters**

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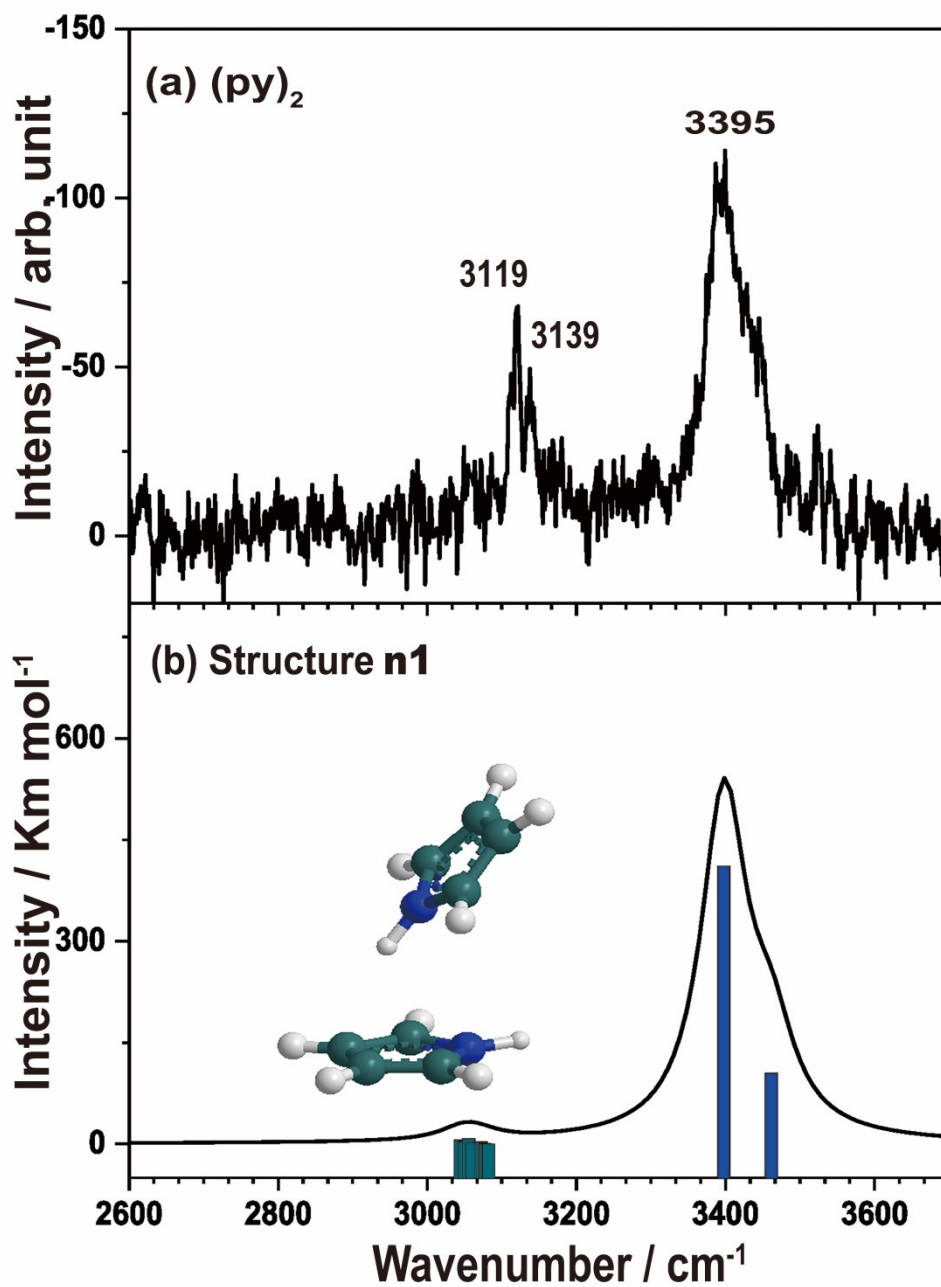
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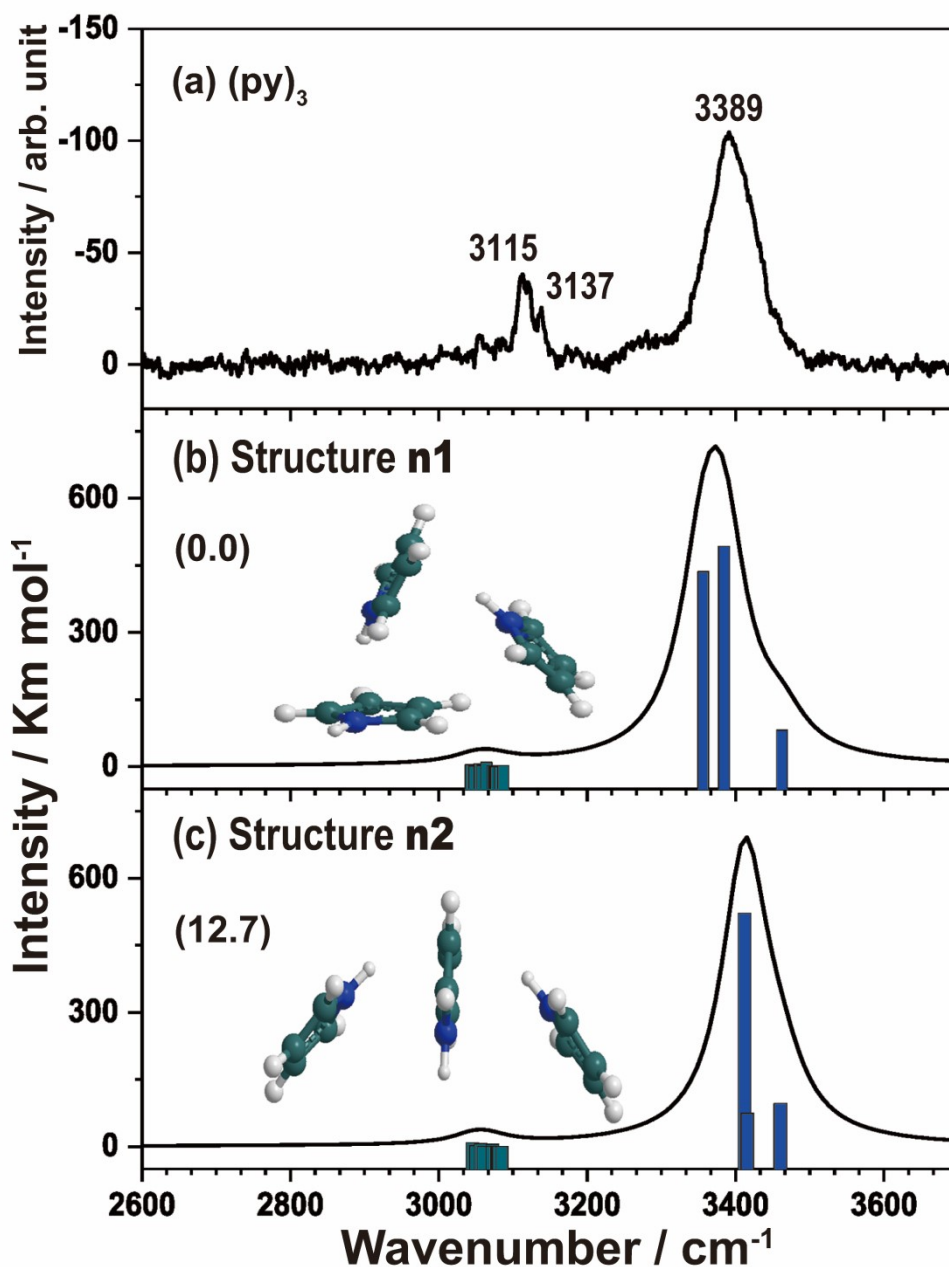
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**Figure S2.** (a) Observed and (b-c) calculated IR spectra of  $(\text{py})_3$ . Frequencies of the two structures were scaled by a factor of 0.943 at B3LYP-D3(BJ)/6-311++G(d,p) level, and the convoluted spectra were obtained by a Lorentzian linewidth function with a width of  $20 \text{ cm}^{-1}$ . The predicted structures and relative energy at the zero point vibrational level (the number in parentheses in  $\text{kJ mol}^{-1}$ ) of the cluster are also shown.

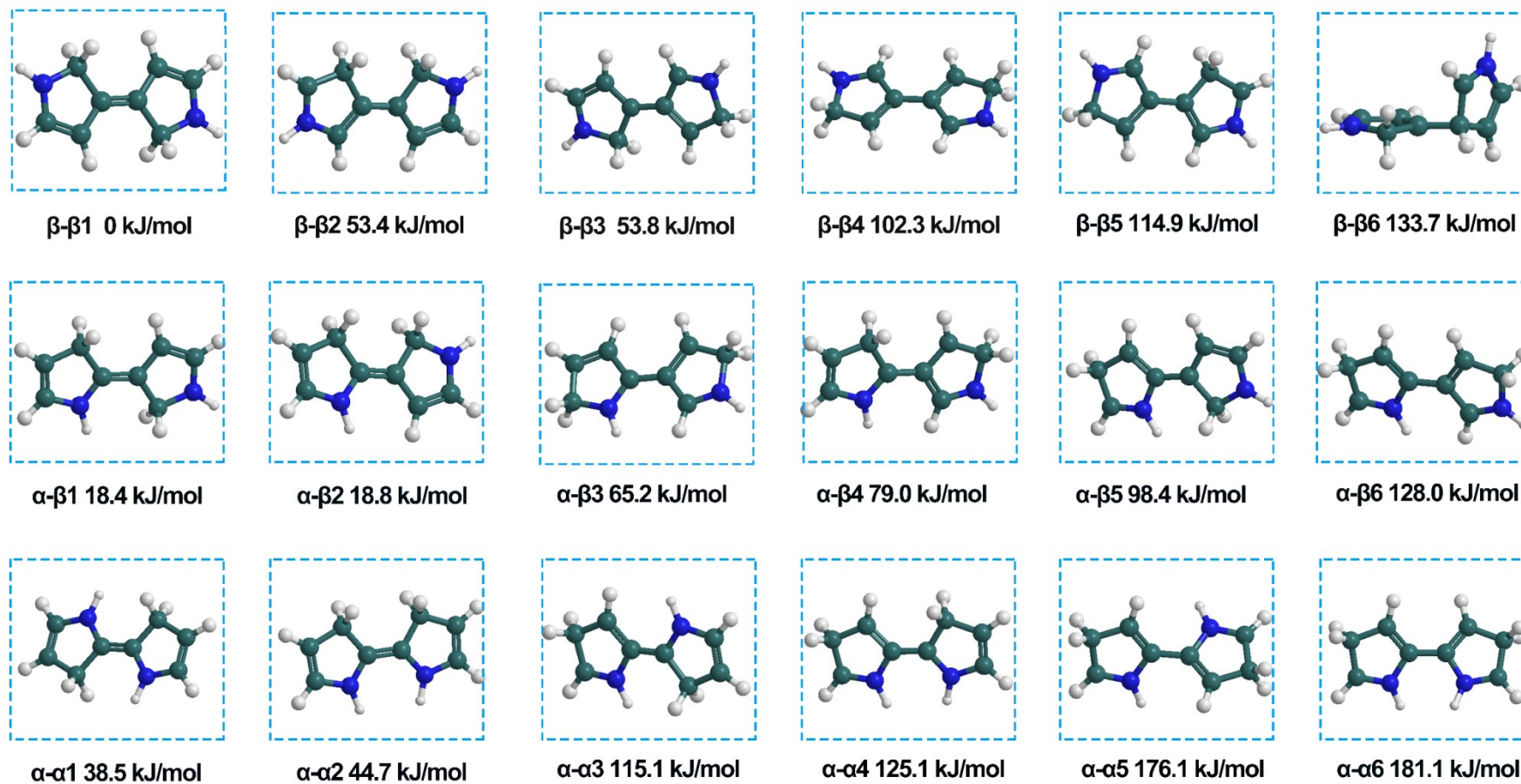
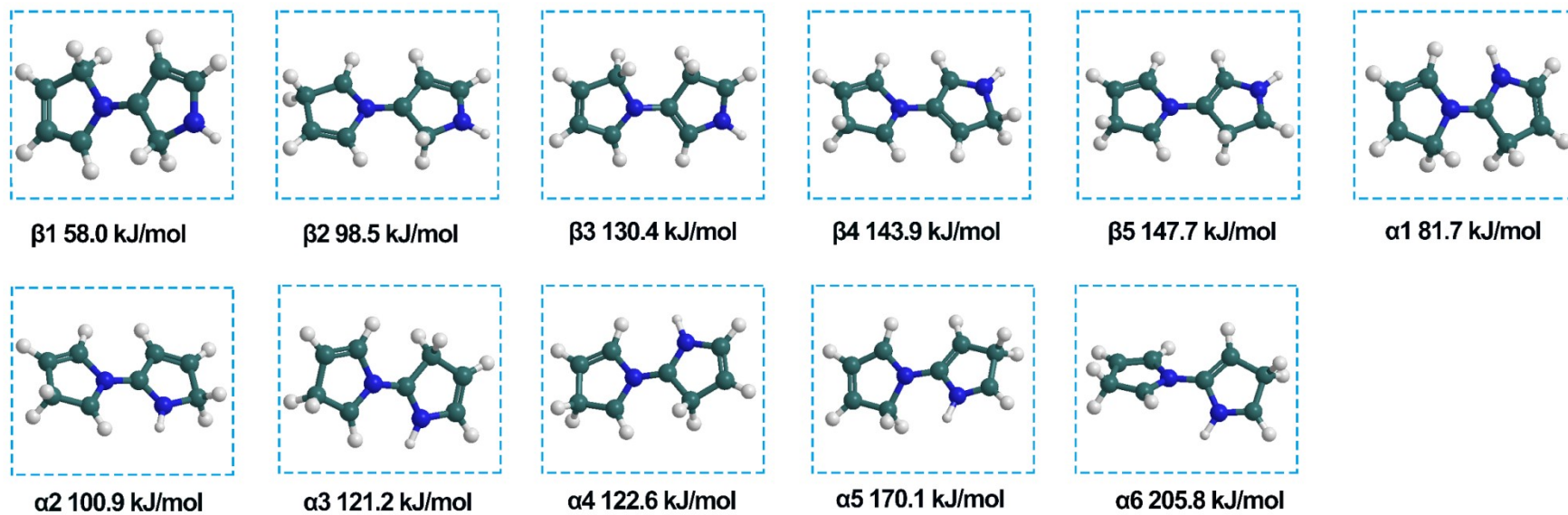
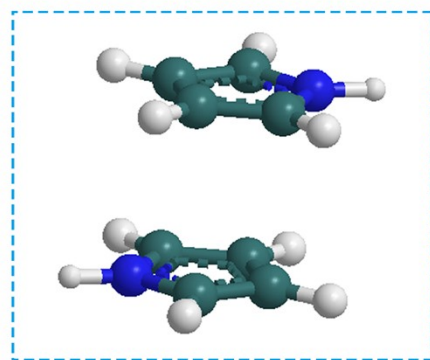


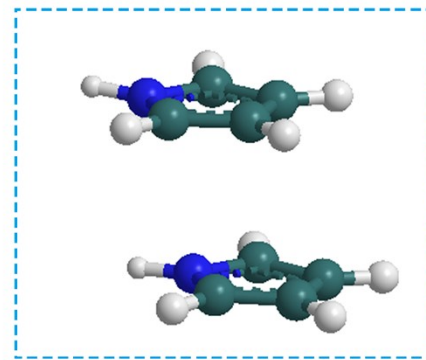
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**Figure S4.** Geometric of eleven stable **cn** type structures of  $(py)_2^+$  predicted with B3LYP-D3(BJ)/6-311++G(d,p) level.

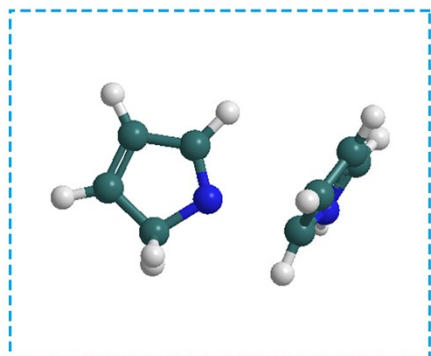


pp1 63.9 kJ/mol

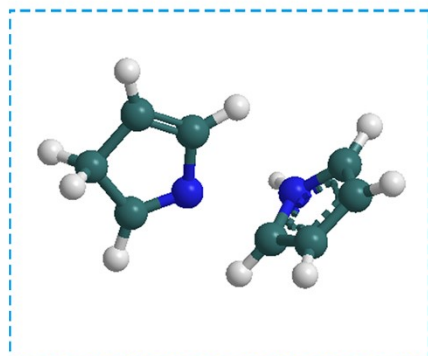


pp2 82.8 kJ/mol

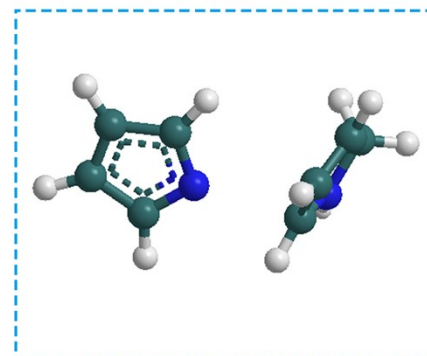
Figure S5. Geometric of two stable **pp** type structures of  $(py)_2^+$  predicted with B3LYP-D3(BJ)/6-311++G(d,p) level.



$n\pi 1$  149.3 kJ/mol



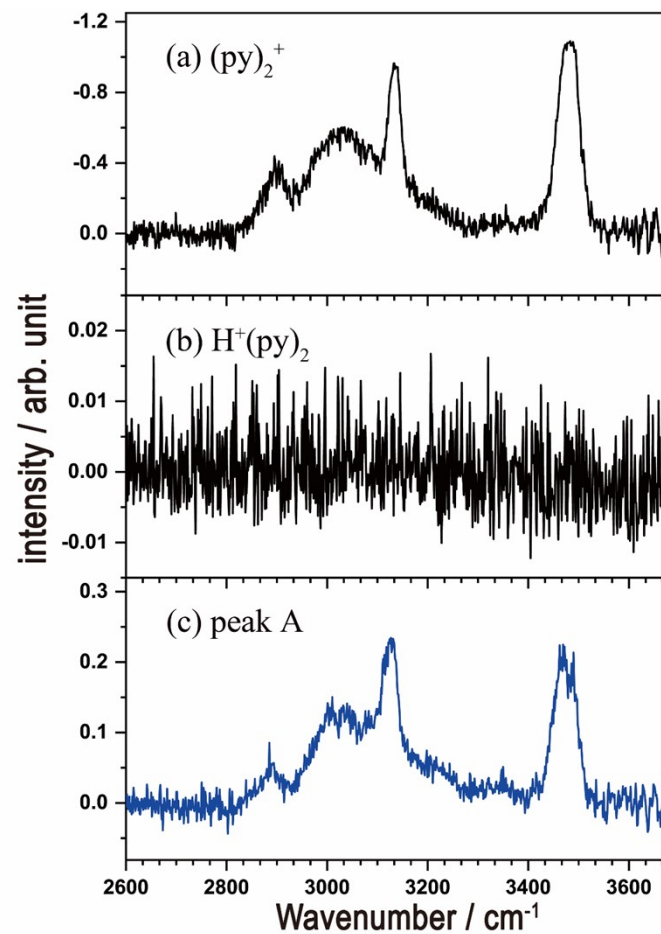
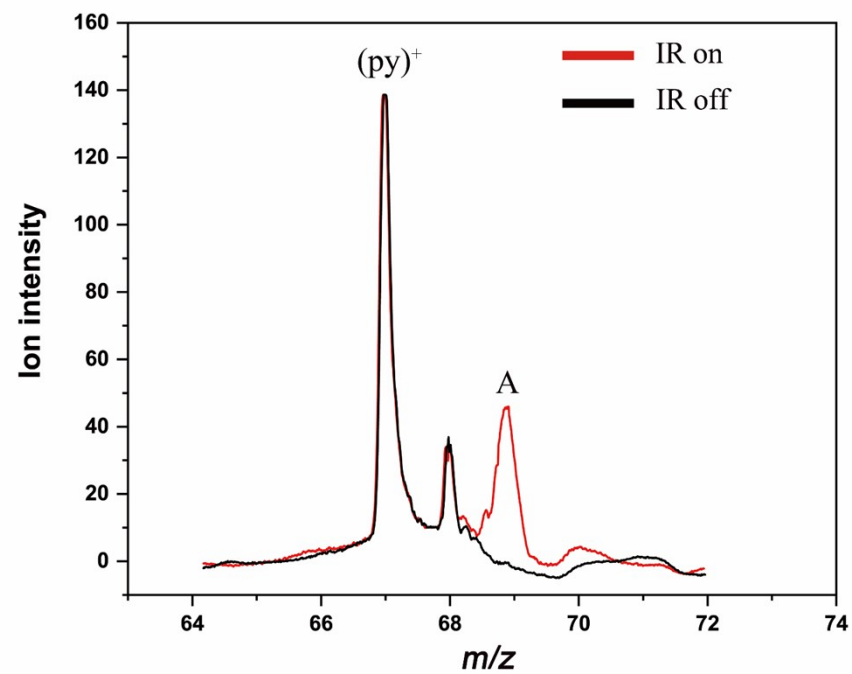
$n\pi 2$  156.9 kJ/mol



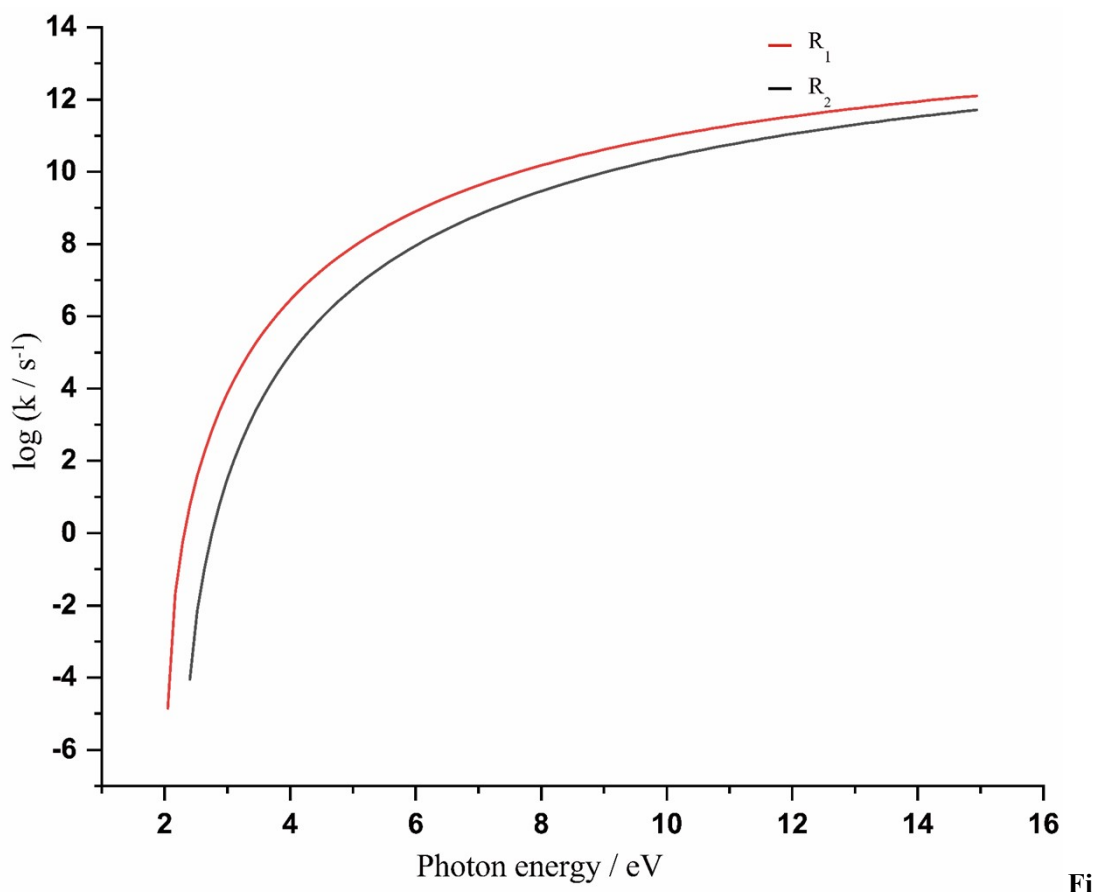
$n\pi 3$  163.0 kJ/mol

**Figure S6.** Geometric of five stable  $n\pi$  type structures of  $(py)_2^+$  predicted with B3LYP-D3(BJ)/6-311++G(d,p) level.





**Figure S7.** (Left panel) Expanded mass spectrum near the  $(py)^+$  region with the IR laser off (black trace) and on (red trace) at  $3480 \text{ cm}^{-1}$ . (Right panel) IR spectra of  $(py)_2^+$ ,  $H^+(py)_2$  and peak A labeled in the mass spectrum. The infrared light is introduced 300ns later than that of VUV light in the ionization region.



**Figure S8.** The calculated RRKM isomerization rate constants for the production of **cc1** ( $R_1$ ) and **cn1** ( $R_2$ ) after ionization as a function of the photon energy.

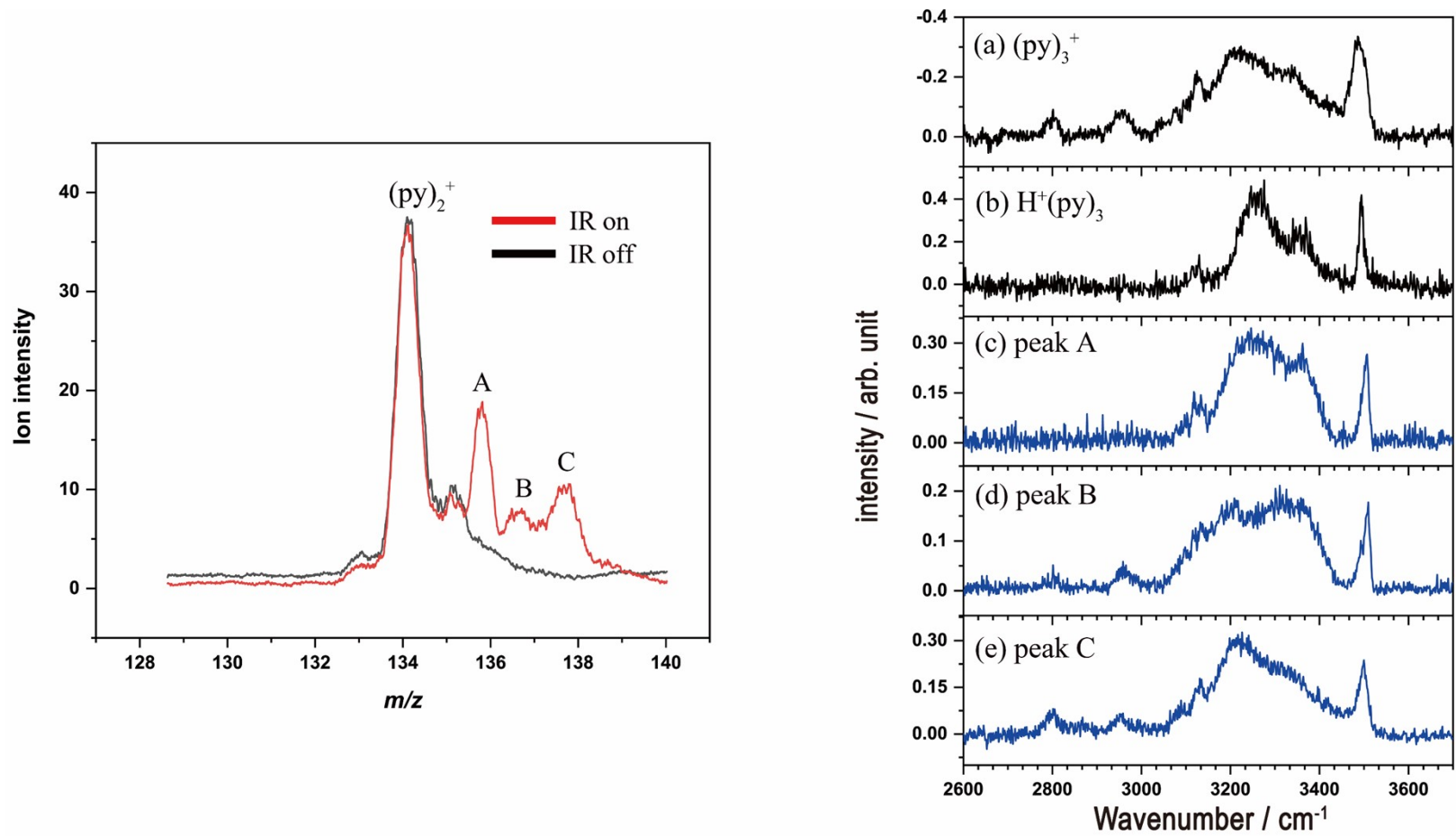
### Computational details of the kinetics stimulation

The internal energy-dependent isomerization rate constants  $R(E)$  of two paths to form covalent bonds were calculated using Rice–Ramsperger–Kassel–Marcus (RRKM) theory.<sup>52,53</sup> The isomerization rate constant with an internal energy  $E$  can be calculated as follows:

$$R(E) = \frac{\sigma N^*(E - E_0)}{h\rho(E)}$$

where  $\sigma$  is the reaction degeneracy,  $N^*(E - E_0)$  represents the total number of states for the activated complex,  $E$  depicts the energy deposited after vertical ionization and  $E_0$  is the energy difference between the transition states and  $AIE$  ( $E_0 = AE - AIE$ ),  $h$  is

Planck's constant and  $\rho(E)$  denotes the density of energized reactant molecule.  $N^*(E - E_0)$  and  $\rho(E)$  are calculated at the harmonic vibrational frequencies using the Beyer-Swinehart algorithm program. The pre-exponential factor is  $A$ , which can be preset in the Masskinetics program<sup>45</sup>, and  $\log A = 15$  is employed in this work. In the following isomerization, the rate constant can be calculated without considering the kinetic energy of the electrons by applying the maximum value of the internal energy of the parent ion ( $E = h\nu - AIE$ ).



**Figure S9.** (Left panel) Expanded mass spectrum near the  $(py)_2^+$  region with the IR laser off (black trace) and on (red trace) at  $3480\text{ cm}^{-1}$ . (Right panel) IR spectra of  $(py)_3^+$ ,  $H^+(py)_3$  and peak A labeled in the mass spectrum. The infrared light is introduced 300ns later than that of VUV light in the ionization region.

**Table S1.** Comparison of observed and scaled harmonic frequencies of  $(py)_2^+$  and their assignments.

Experiment		Calculation <sup>[a]</sup>			Assignments
Bands (cm <sup>-1</sup> ) <sup>[b]</sup>	<b>cc1</b>	<b>cn1</b>	<b>pp1</b>	<b>nπ1</b>	
2887	2881 (3.2) <sup>[c]</sup>	2886 (5.6)		2891(3.3)	s-CH <sub>2</sub> -stretch
		2873 (5.5)			
3011	2911 (1.5)	2920 (0.4)			a-CH <sub>2</sub> -stretch
		2904 (0.6)			
3129	3077 (18.4)	3082 (1.5)	3100 (15.7)	3071 (2.5)	a-CH-stretch
		3080 (19.9)	3090 (0.8)	3090 (1.1)	
				3093(1.1)	
				3101 (9.2)	
3470	3095 (4.8)	3108 (6.9)	3114 (0.5)	3121 (1.8)	s-CH-stretch
		3106 (14.1)	3108 (18.7)	3109 (11.1)	
		3095 (4.9)			
3470	3473 (607.4)	3479 (296.1)	3470 (297.5)	3465 (144.7)	free NH-stretch

<sup>[a]</sup> calculated at B3LYP-D3(BJ)/6-311++G(d,p) level and scaled by a factor of 0.954. <sup>[b]</sup> wavenumbers of the bands in the IR spectra of  $(py)_2^+$ . <sup>[c]</sup> the value in the parentheses is IR intensities in km mol<sup>-1</sup>.

**Table S2.** Comparison of observed and scaled harmonic frequencies of (py)<sub>3</sub><sup>+</sup> and their assignments.

Experiment	Calculation <sup>[a]</sup>				Assignments
	(cc1) <sup>+</sup> py	(cn1) <sup>+</sup> py	(pp1) <sup>+</sup> py	(nπ1) <sup>+</sup> py	
Bands (cm <sup>-1</sup> ) <sup>[b]</sup>					
2793	2881 (1.9) <sup>[c]</sup>	2882 (7.0) 2880 (10.0)		2889 (2.5)	s-CH <sub>2</sub> -stretch
2943	2876 (4.0)	2912 (2.0)			a-CH <sub>2</sub> -stretch
	2905 (2.0)				
	3079 (3.0)	3095 (4.5)	3108 (7.0)	3099 (4.6)	a-CH-stretch
	3079 (1.0)	3081 (2.1)	3106 (2.4)	3027 (4.2)	
	3077 (11.1)	3076 (9.3)	3101 (5.1)	3091 (0.8)	
			3099 (2.2)		
			3093 (0.5)		
broad feature	3095 (1.4)	3107 (10.1) 3107 (5.3)	3116 (3.6) 3115 (0.4)	3129 (1.6) 3109 (8.2)	s-CH-stretch
	3095 (1.3)				
	3104 (0.7)	3104 (0.9)	3098 (2.9)	3078 (1.1)	H-bonded a-CH-
	3089 (0.2)	3089 (0.3)	3085 (1.2)	3104 (1.4)	stretch of third C <sub>4</sub> H <sub>5</sub> N
		3079 (0.8)	3073 (0.5)		
	3109 (0.1)	3108 (0.1)	3104 (1.2)	3109 (0.4)	H-bonded s-CH-
					stretch of third C <sub>4</sub> H <sub>5</sub> N
3488	3484 (92.3)	3482 (97.9)	3476	3480 (106)	free NH-stretch
	3481 (288.9)		(102.1)		
		3231	3309		H-bonded NH-stretch
	3249 (1908.1)	(1775.9)	(1249.7)	3210	
			3281 (131.8)	(1073.7)	

<sup>[a]</sup> calculated at B3LYP-D3(BJ)/6-311++G(d,p) level and scaled by a factor of 0.954. <sup>[b]</sup> wavenumbers of the bands in the IR spectra of (py)<sub>2</sub><sup>+</sup>. <sup>[c]</sup> the value in the parentheses is IR intensities in km mol<sup>-1</sup>.

**Table S3.** The simulated spectra of the three isomers for  $(py)_2^+$  were calculated at B3LYP-D3(BJ)/6-311++G(d,p) level and their assignments.

Isomers	Fundamental Freq. ( $cm^{-1}$ )	Intensity ( $Km$ $mol^{-1}$ )	Assignments	Overtone Freq. ( $cm^{-1}$ )	Intensity ( $Km$ $mol^{-1}$ )	Assignments
<b>pp1</b>	3117	1.3	Fund (45)	2671	0.0	Over (37 <sup>2</sup> )
	3118	0.0	Fund (46)	2703	0.0	Over (38 <sup>2</sup> )
	3126	0.6	Fund (47)	2707	0.0	Over (39 <sup>2</sup> )
	3127	11.4	Fund (48)	2802	0.0	Over (40 <sup>2</sup> )
	3133	0.3	Fund (49)	2950	0.0	Over (41 <sup>2</sup> )
	3134	11.7	Fund (50)	2965	0.0	Over (42 <sup>2</sup> )
	3140	0.0	Fund (51)	2961	0.0	Over (43 <sup>2</sup> )
	3141	0.0	Fund (52)	2982	0.0	Over (44 <sup>2</sup> )
<b>cc1</b>	2901	0.0	Fund (45)	2829	0.0	Over (38 <sup>2</sup> )
	2909	2.0	Fund (46)	2849	0.0	Over (39 <sup>2</sup> )
	2904	2.2	Fund (47)	2952	0.0	Over (40 <sup>2</sup> )
	2905	1.1	Fund (48)	2963	0.0	Over (41 <sup>2</sup> )
	3107	11.1	Fund (49)	2978	0.0	Over (42 <sup>2</sup> )
	3109	1.4	Fund (50)	3001	0.0	Over (43 <sup>2</sup> )
	3127	4.7	Fund (51)	3141	0.0	Over (44 <sup>2</sup> )
	3128	0.3	Fund (52)			
<b>cn1</b>	2891	2.3	Fund (45)	2728	0.1	Over (37 <sup>2</sup> )
	2909	2.1	Fund (46)	2793	0.8	Over (38 <sup>2</sup> )
	2898	1.5	Fund (47)	2833	0.0	Over (39 <sup>2</sup> )
	2916	1.1	Fund (48)	2848	0.7	Over (40 <sup>2</sup> )
	3109	4.4	Fund (49)	2944	0.6	Over (41 <sup>2</sup> )
	3094	1.7	Fund (50)	2970	2.1	Over (42 <sup>2</sup> )
				2992	0.4	Over (43 <sup>2</sup> )
				3084	9.8	Over (44 <sup>2</sup> )