

Electronic Supplemental Information

***In-situ* Raman monitoring of [2+2] cycloaddition of pyridine substituted olefins induced by visible laser**

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1. Experimental Section

Materials and reagents

4-vinylpyridine (4-VP) and (BPE) were purchased from the Aladdin reagent, used without further purification. Silver (I) trifluoroacetate was purchased from Sigma-Aldrich. Methanol, tetrahydrofuran (THF) and n-hexane were purchased from Sinopharm Chemical Reagent Co., Ltd.

The preparation of crystalline [Ag₂(4-VP)₄][TFA]₂ (4-VP = 4-vinylpyridine, TFA = trifluoroacetate) (Crystal 1)

Crystalline [Ag₂(4-VP)₄][TFA]₂ (where 4-VP = 4-vinylpyridine, TFA = trifluoroacetate) **1** was prepared according to the method previously published.¹ 4-VP with silver trifluoroacetate with mole ratio 2:1 methanol solution mixed. White precipitate (PVP, poly(4-vinylpyridine)) was filtered. After 1 day, the transparent crystal was collected and used in the Raman experiments. The sample can even be dropped on the slide, and the solid crystalline sample was obtained after the solvent evaporated.

The preparation of crystalline [Ag₂(PEA)₄][TFA]₂ (PEA = Ethyl-(pyridine-4-yl)prop-2-enolate) (Crystal 2)

The crystalline sample was prepared with the literature method modified.² Silver trifluoroacetate (0.048g, 0.57mM) and PEA (0.1g, 0.57mM) with 1:1 mole ratio were dissolved in the methanol solution. Needle crystal was filtered after 2 days. Crystal sample was collected 0.05g, yield: 34%.

The preparation of cocrystal (BPE)₂·(RES)₂ (BPE = *trans*-1,2-bis(4-pyridyl)-ethylene, RES = resorcinol) (Crystal 3)

The **BPE** with **RES** cocrystal were prepared with liquid-liquid layer diffusion method. The THF solution containing the **BPE** and **RES** equimolar mixed and transferred into the bottom of tube, then layered with n-hexane. After three days, transparent crystal was collected.

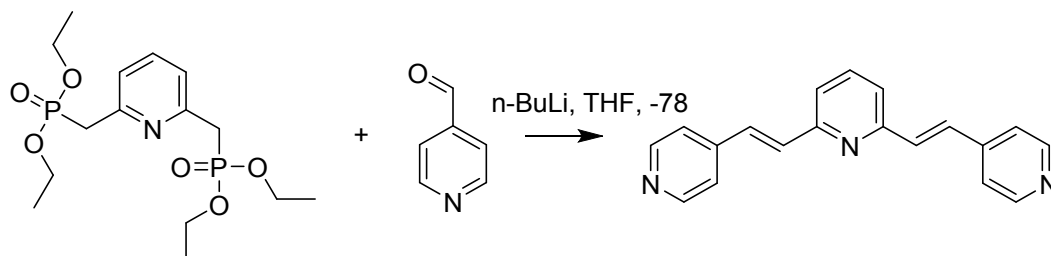
The preparation of cocrystal (BPEP)₂·(RES)₂ (BPEP = 1,3-bis(*trans*-4-pyridylethylenyl)pyridine) (Crystal 4)

Cocrystal 1,3-bis(*trans*-4-pyridylethylenyl)pyridine (68.6 mg, 0.24 mmol) and resorcinol (26.47 mg, 0.24 mmol) in 1:1 ratio was dissolved in 5ml THF and transferred into the bottom of tubes, layered with n-Hexane. After 3 days, yellow single crystals suitable for X-ray diffraction was collected, and dried at room temperature (41 mg, 43.1% yield).

The synthesis of 1,3-bis(*trans*-4-pyridylethylenyl)pyridine (BPEP)

Though BPEP can be prepared through Suzuki reaction method,³ it was synthesized through Wittig-Horner reaction in this paper. Tetraethyl 2,6-bis(methanephosphonate)pyridine (1.0 g, 2.64 mmol) was dissolved in 15mL anhydrous THF under a nitrogen atmosphere, and placed in the iced bath for 15min. 2.75 ml n-BuLi (2.4M, 6.59 mmol) was added dropwise. The flask was moved out and stirred for another 0.5h at room temperature. 4-pyridinealdehyde (0.55 mL, 5.8 mmol) in 5mL anhydrous THF was added dropwise. The reaction was stirred overnight. The reaction was quenched with water, extracted twice with 15 mL Ethyl acetate. The combined organic layer was washed with water (15mL), saturated brine (15mL), and dried with anhydrous sodium sulfate. The dry solution was passed through a silica gel column using Ethyl acetate/methanol = 1:1(v/v) as eluent. The solvent was evaporated to yield a white solid (4.10 g, 72% yield).^{4,5}

¹H NMR: (400 MHz. CDCl₃. ppm); δ 8.60 (d, 4H, J=4Hz), 7.69 (t, 2H, J=8Hz), 7.65 (d, 2H, J=16), 7.43 (d, 4H, J=4), 7.36 (d, 2H, J=16), 7.32(d, 2H, J=8); ¹³C NMR: (100 MHz. CDCl₃. ppm); δ 154.46, 150.33, 143.92, 137.39, 132.23, 130.54, 122.11, 121.35. HRMSESI m/z: calcd for [M + H]⁺ 286.1339, found 286.1341; calcd for [2M + H]⁺ 571.2605, found 571.2608.



Ethyl-(pyridine-4-yl)prop-2-enotate (PEA)

The PEA was synthesized through Wittig-Horner Reaction. Triethyl phosphonoacetate (1mL, 5mM) treated with excess n-BuLi (0.57mL, 6.1mM) at -78 centigrade degrees for one and half an hours, and then it was warmed up in air for 0.5 hour. 4-pyridinecarboxaldehyde (0.48mL, 5.1mM) was added drop wise within 0.5 hour. The reaction was monitored with TLC. After the reaction was completed, it was quenched with 10 mL brine. The product was purified through column chromatography with ethyl acetate: petroleum=1:4 (v/v). 0.81 g yield: 91%. ¹H NMR: (400 MHz. CDCl₃. ppm); δ 1.351(d, 3H, J = 7Hz, CH₃ of Et); δ 4.264(m, 2H, J = 7Hz, -COOCH₂); δ 6.575(d, 1H, J = 7Hz, Py-CH=); δ 7.359(d, 2H, J = 7Hz, Py-βH); δ 8.649(d, 2H, J = 7Hz, Py-αH); ¹³C NMR: (100 MHz. CDCl₃. ppm); δ 14.254, 60.965, 124.774, 122.918, 141.658, 150.611, 166.013.

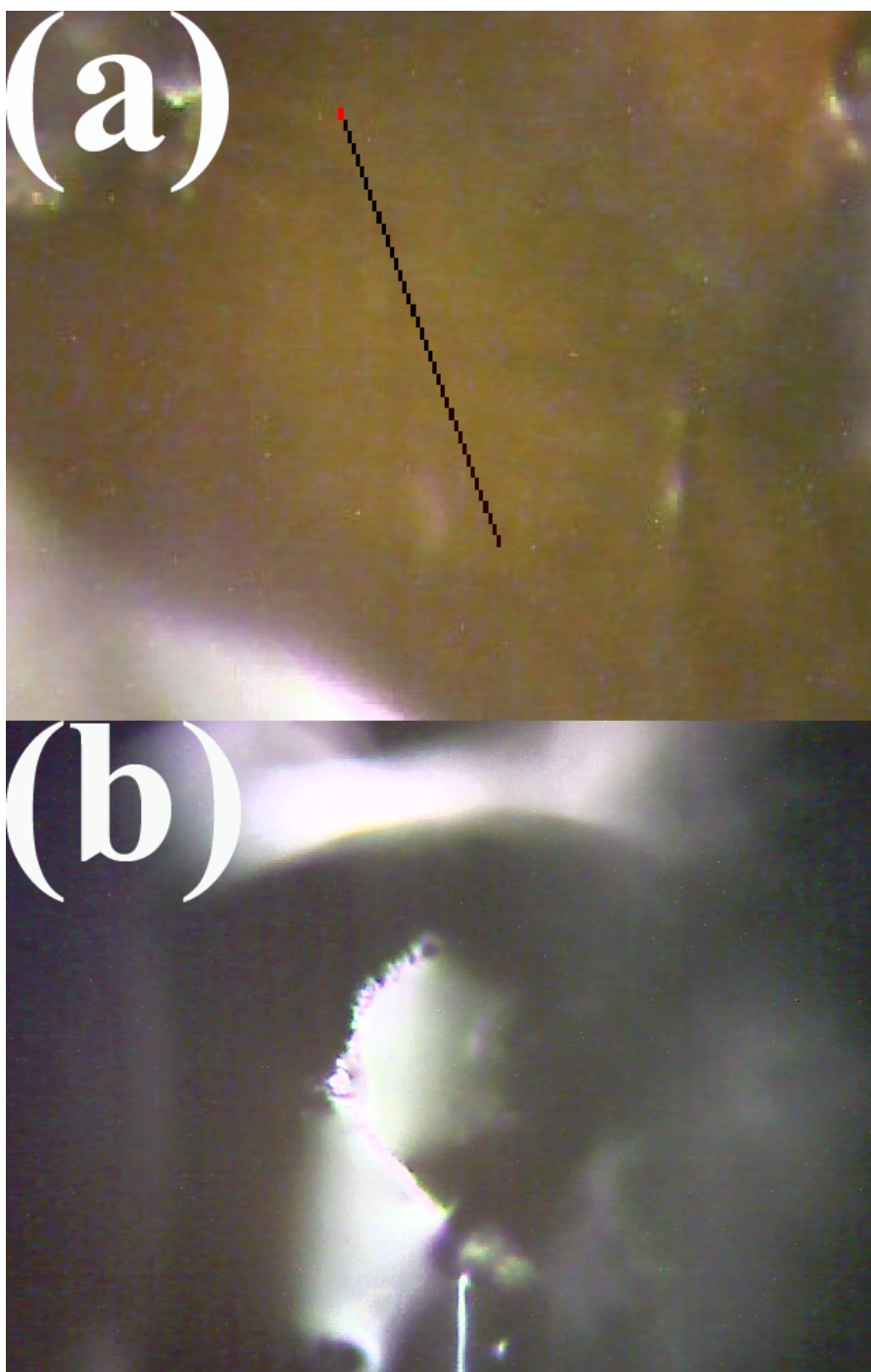


Fig. S1: Optical images of crystal **1** before (a) and after (b) scanned with 100% laser power (633nm).

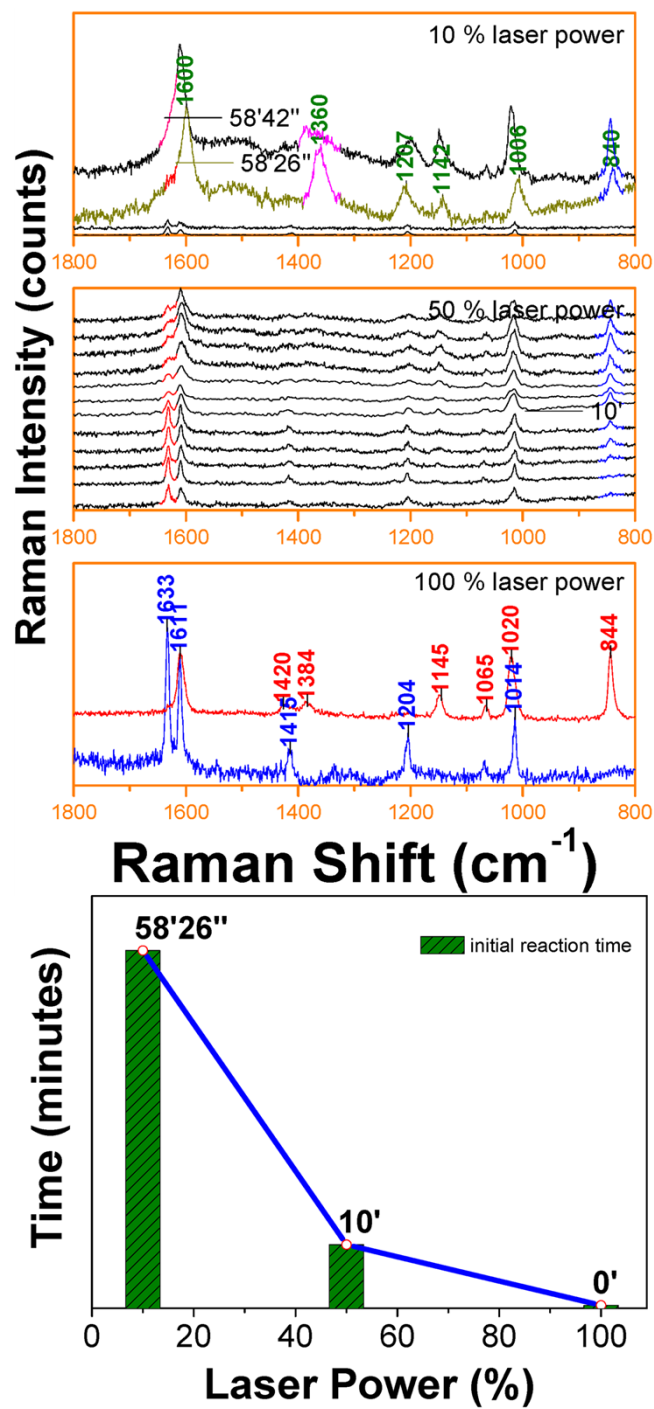


Fig. S2: The Raman spectra of 1 under 633 nm laser with different power (10%, 50%, 100%) irradiation, and their initial reaction time plots.

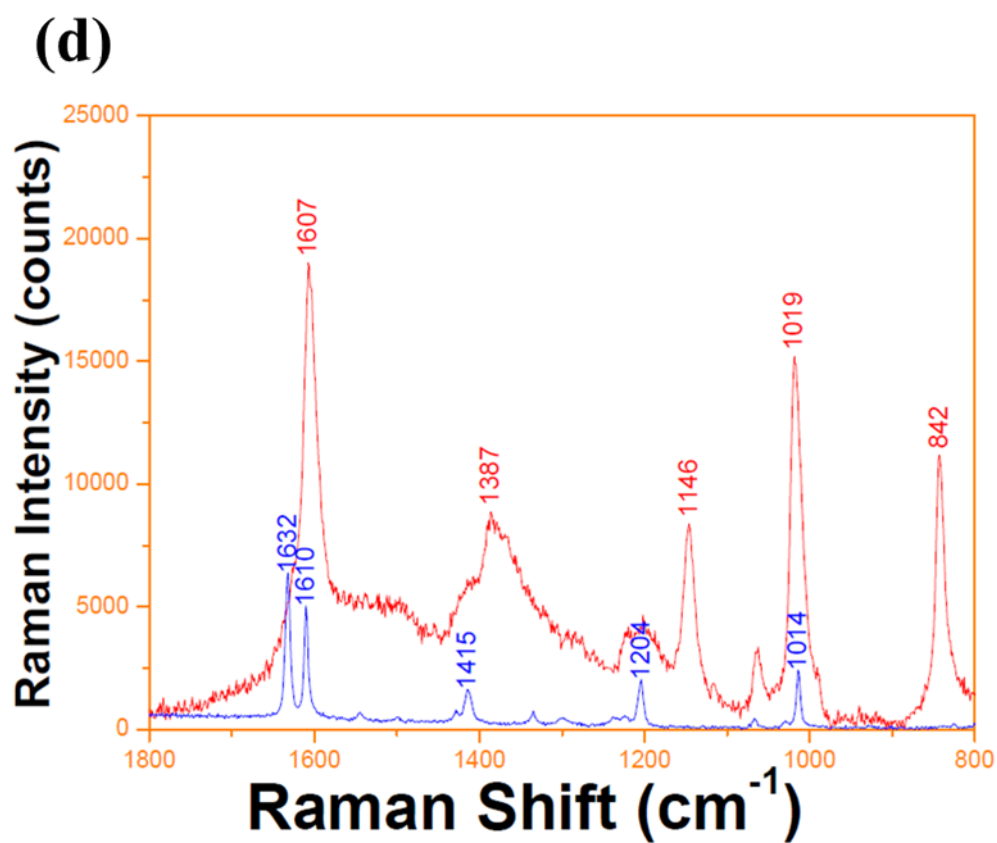
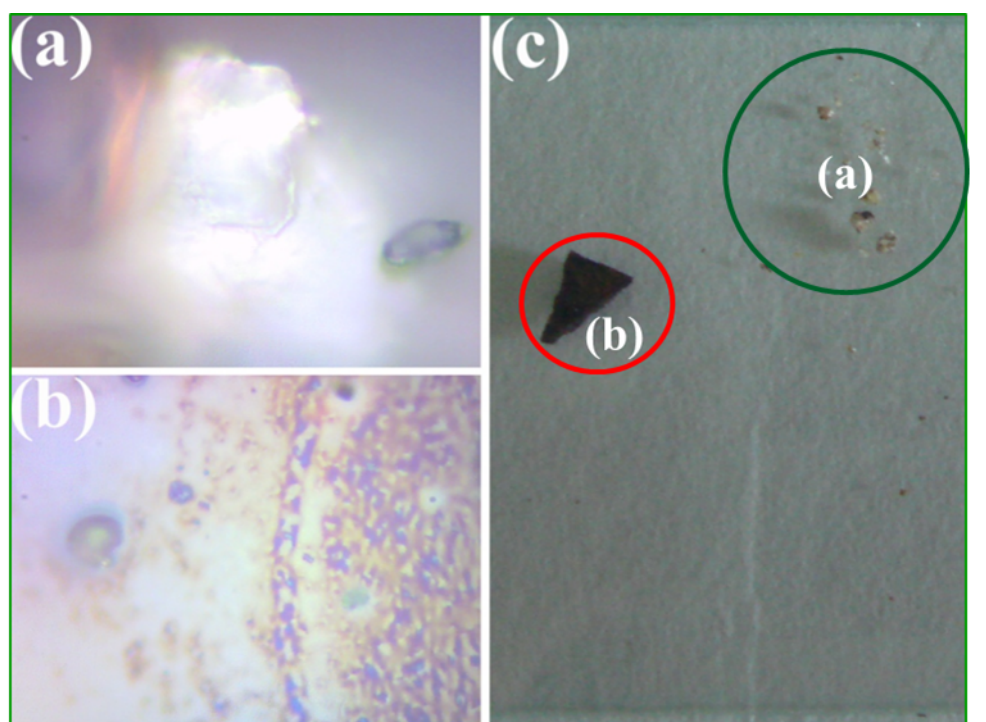


Fig. S3: The crystal **1** was irradiated with high pressure mercury lamp as UV light source for 78 hours. Optical images of sample **1** at the unreacted (a) and reacted (b) area; (c) the black sample circled with red line is irradiated with UV, the circled with blue line sample is unreacted sample. (d) The Raman spectra were taken from the unreacted area (blue line) and reacted area (red line) with UV irradiation for 78 hours.

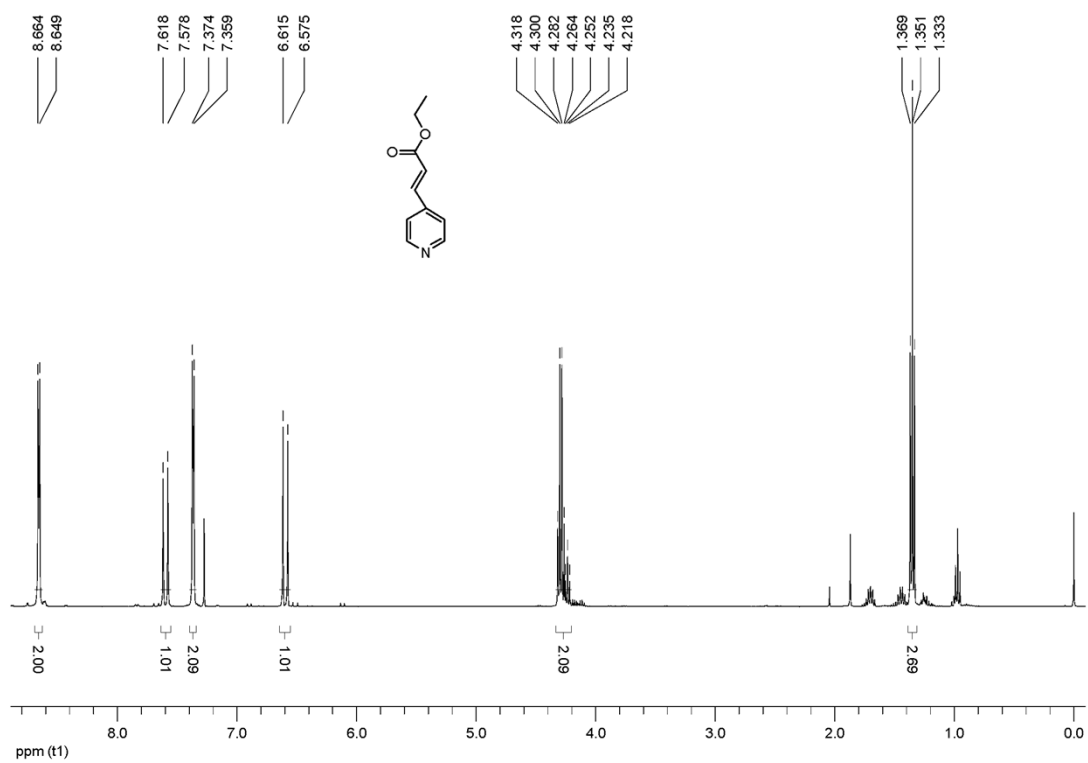


Fig. S4: ¹H NMR of Ethyl-(pyridine-4-yl)prop-2-enotate (PEA).

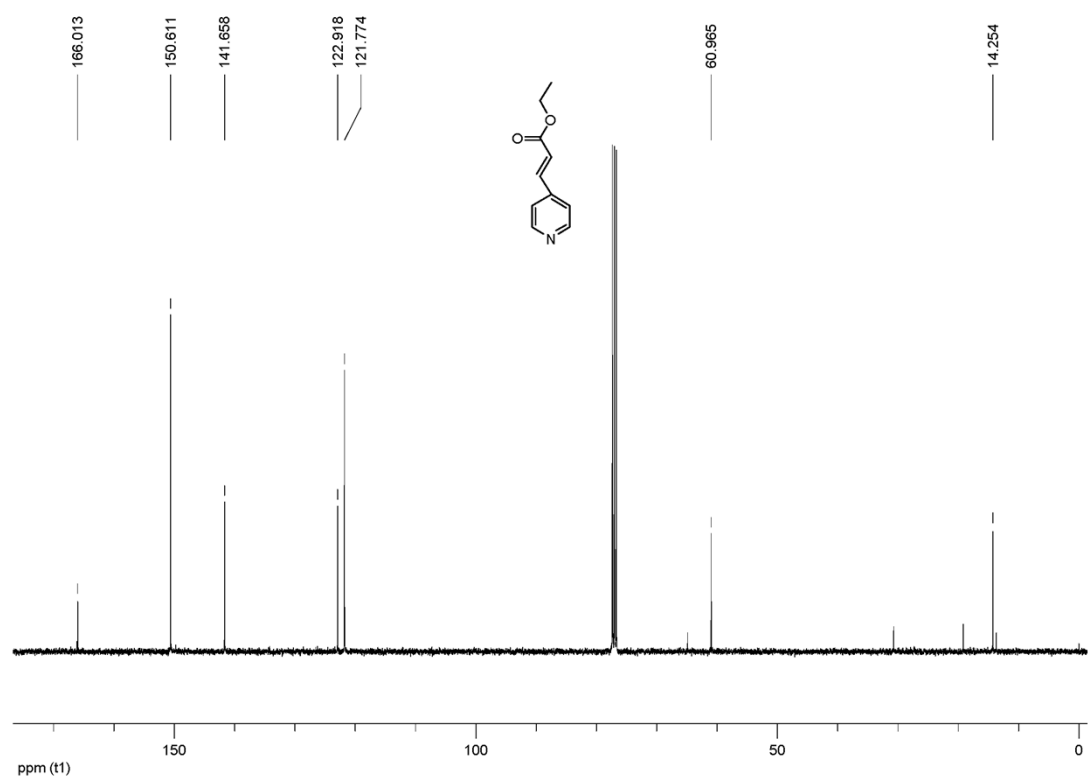


Fig. S5: ¹³C NMR of Ethyl-(pyridine-4-yl)prop-2-enotate (PEA).

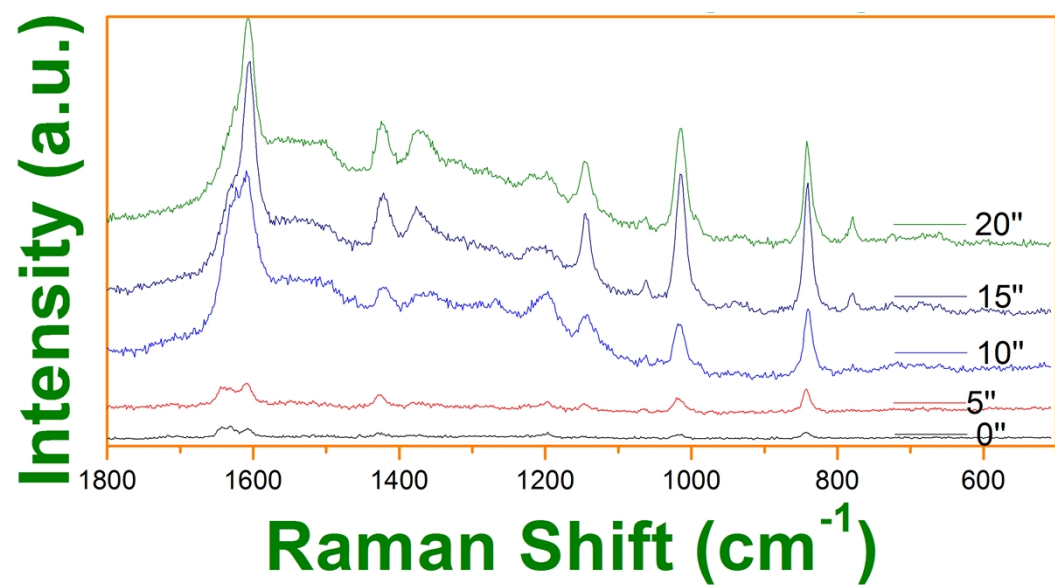
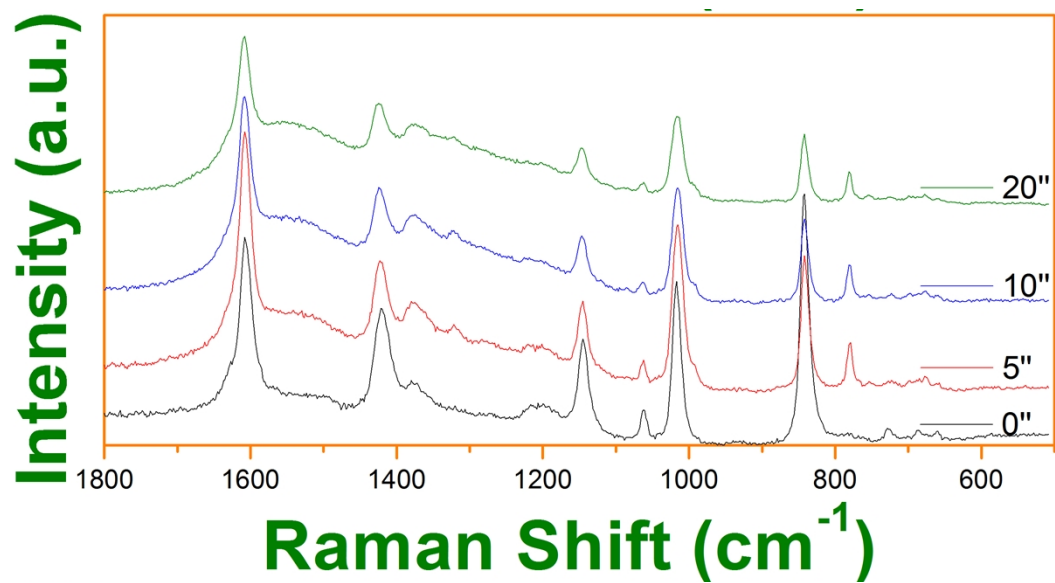


Fig. S6: Time-dependent Raman spectra of crystal **1** (up) and **2** (down) under 532 nm laser excitation with 1.18 mW power.

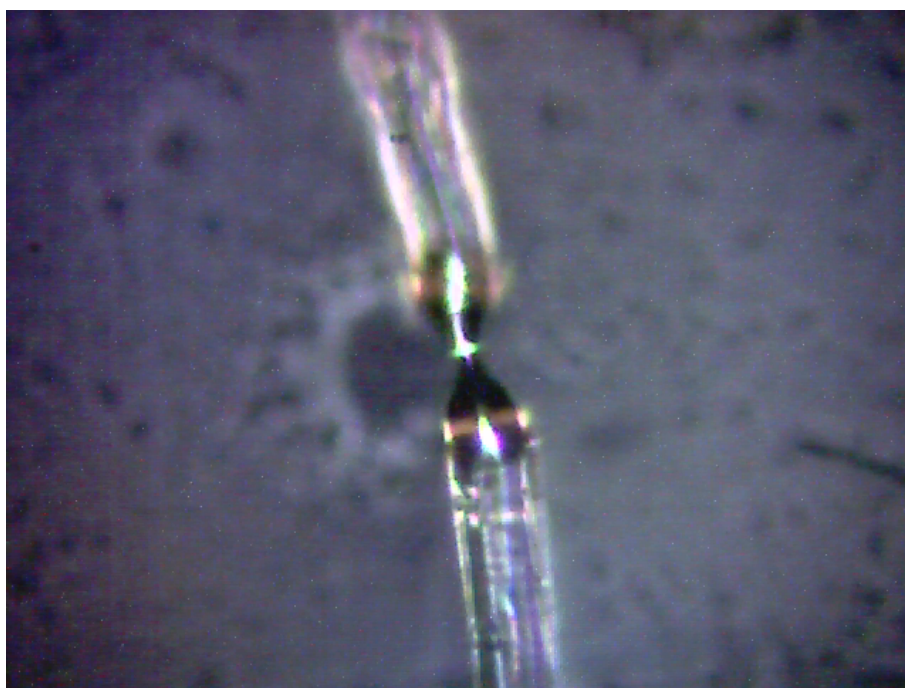
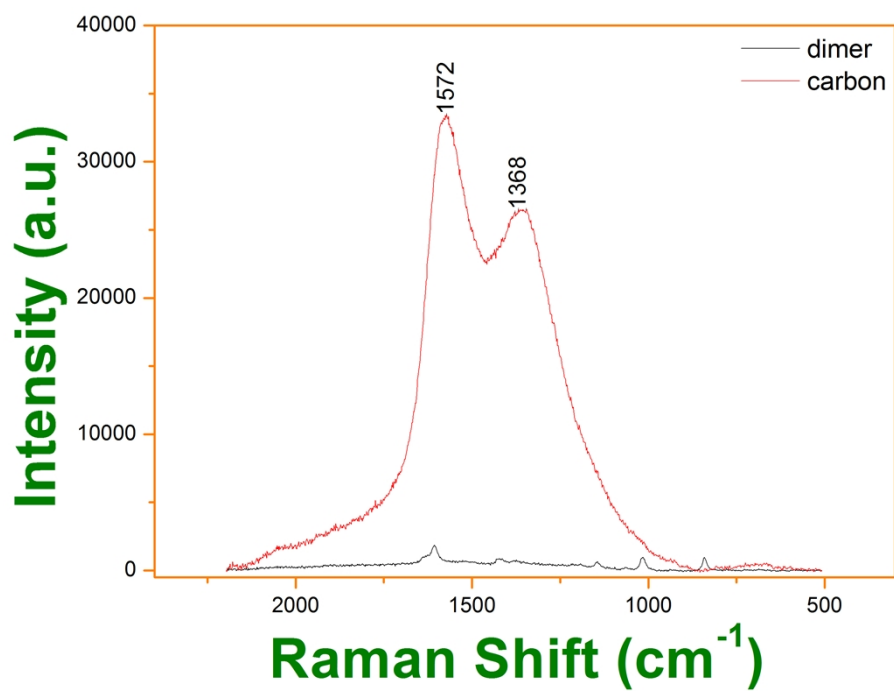


Fig. S7: Raman spectrum of crystal **2** (up) under 532 nm laser excitation with 6.35 mW power for only 1 s and the corresponding optical image of the crystal. The 1368 and 1572 cm⁻¹ in the Raman spectrum can be assigned to the D and G bands of carbon materials.

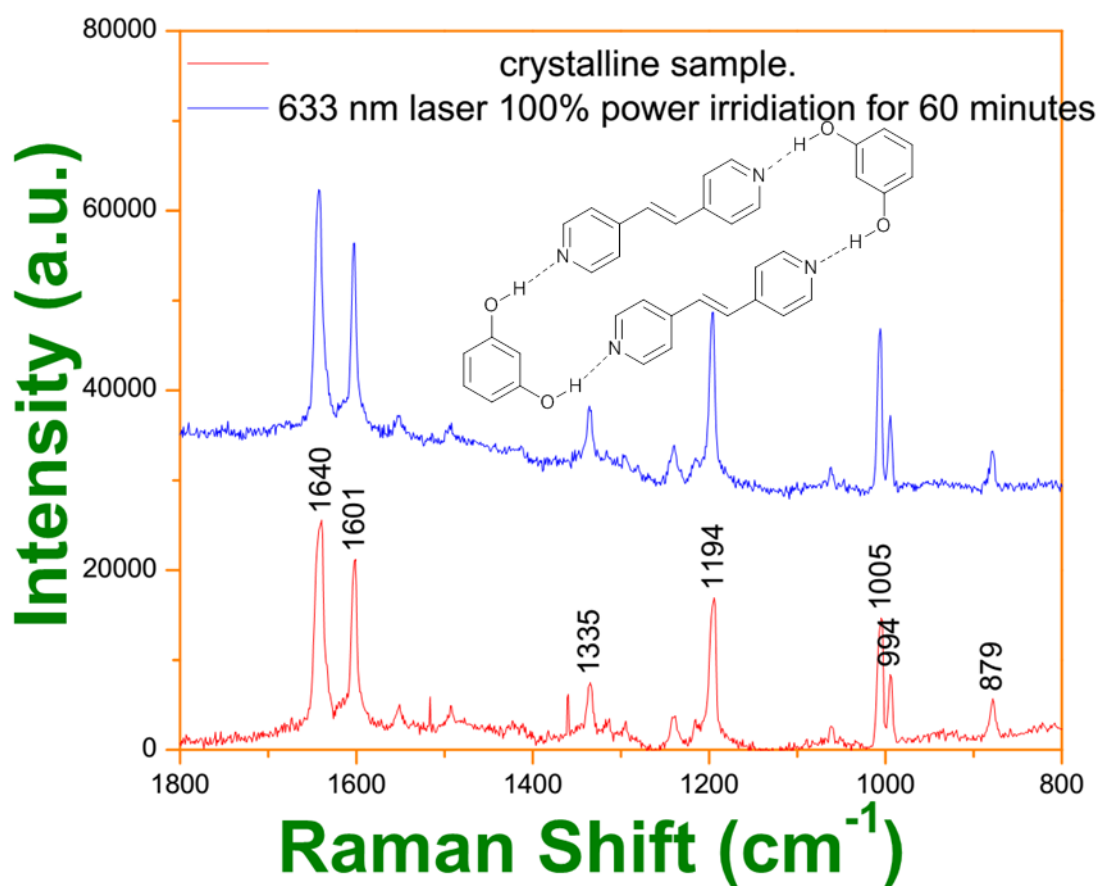


Fig. S8: Raman spectrum of crystal **3** (red line); there were no changes even under 100% laser power irradiation for 60 minutes (blue line). Even using 532 nm laser with 100% power, there were no changes.

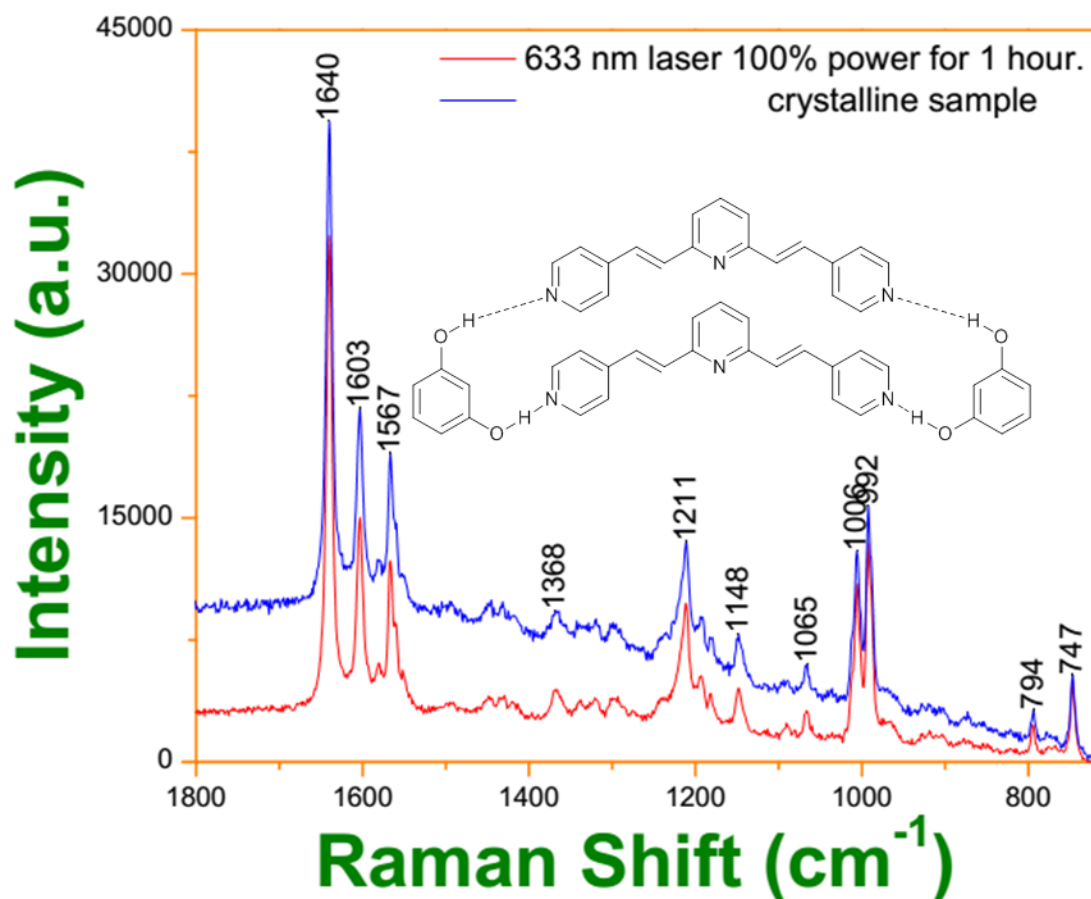


Fig. S9: Raman spectra of crystalline **4** (blue line); there are no changes under 633 nm laser irradiation for 60 minutes (red line). Even using 532 nm laser, there were still no changes.

References:

1. I. G. Georgiev, D. K. Bucar and L. R. MacGillivray, *Chem. Commun.*, 2010, **46**, 4956-4958.
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