Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Facile light-initiated radical generation from 4-substituted pyridine under ambient conditions

Ami Nakayama, Haru Kimata, Kazuhiro Marumoto, Yohei Yamamoto and Hiroshi Yamagishi*

Department of Materials Science, Faculty of Pure and Applied Sciences, and Tsukuba Research Center for Energy Materials Science (TREMS) University of Tsukuba 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8573, Japan.

*Correspondence and requests for materials should be addressed to Hiroshi Yamagishi (yamagishi.hiroshi.ff@u.tsukuba.ac.jp).

Table of Contents

1. Materials

Commercial reagents were purchased from Sigma-Aldrich, TCI, and Wako Pure Chemical Industries, Ltd. Ionic salts ($TEABF_4$, $TEANO_3$, $TMABF_4$, and $NaBF_4$) were recrystallized prior to use. **Py_6Mes** was synthesized according to the previous literature [S1] and recrystallized from acetonitrile prior to use.

2. General

Light irradiation was conducted with a Hamamatsu model LC-L1V5 UV-LED spot light source. Thermogravimetric analysis (TGA) was conducted on a Seiko Instruments Inc. model EXSTAR7000：TG/DTA7300 in a temperature range from 40 to 210 °C at a heating rate of 5 °C min^{-1} under constant Ar flow. ^1H NMR spectra were recorded on a JEOL JMTC-400/54/SS and on a Bruker AVANCE-400 spectrometers (^1H NMR, 400 MHz) using residual DHO signal as an internal standard. Powder X-ray diffraction (XRD) patterns were recorded on a RIGAKU model Miniflex600 diffractometer with a Cu$K\alpha$ radiation source (40 kV and 15 mA), equipped with a model D/Tex Ultra2-MF high-speed 1D detector. The PXRD data were collected in a range from 3 to 30° in 2θ by a step-scan mode with a step size of 0.01°. Fourier-transform infrared (FT-IR) spectra were acquired on a JASCO model FT/IR-4200 Spectrometer equipped with an ATR PRO450-S single reflection ATR accessory. Electronic absorption spectra were recorded on a JASCO model V-570 UV/VIS/NIR spectrometer. Diffuse reflectance spectra were recorded on JASCO model V-570 UV/VIS/NIR spectrometer equipped with a JASCO model ISN-470 integrating sphere option. The measurement procedures and the detailed information of the apparatus of Electron Spin Resonance (ESR) spectroscopy are written in the following section.

3. Thermogravimetric Analysis

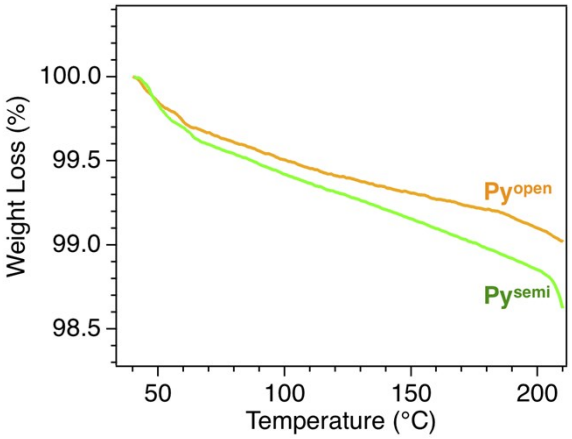

Figure S1. TGA profiles of **Py^{open}** (orange curve) and **Py^{semi}** (green curve). Each sample was dried for 2 h under reduced pressure prior to the measurements.

4. NMR Spectroscopy

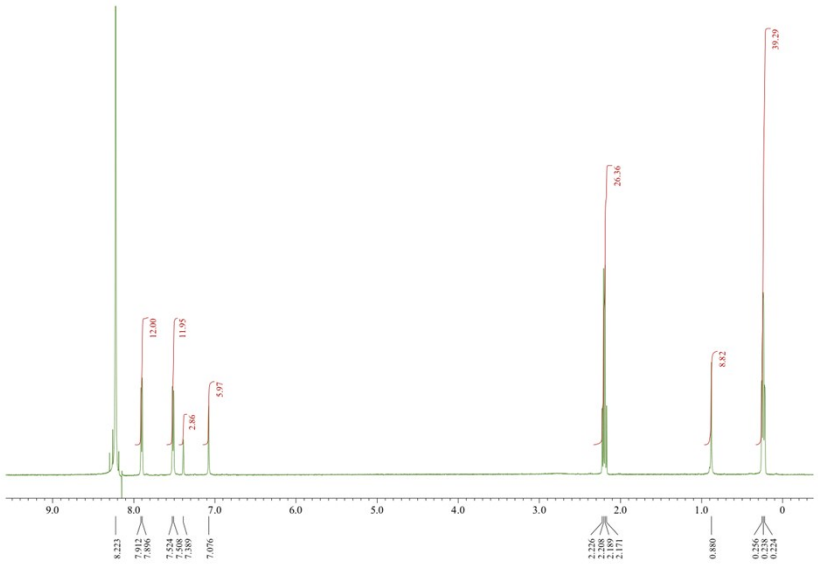

Figure S2. ^{1}H NMR spectrum of **Py^{semi}** in 35 wt% D_2O solution of DCl.

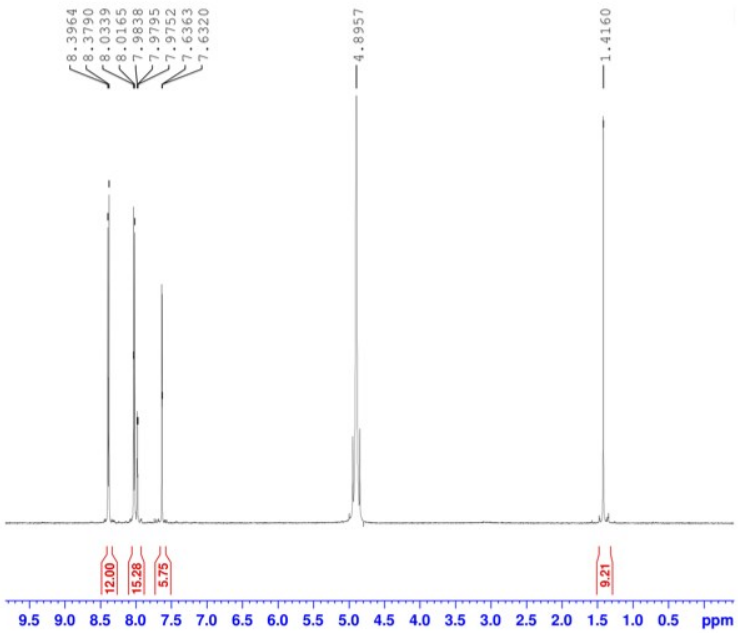

Figure S3. ^{1}H NMR spectrum of **Py$_6$Mes** in 5 wt% D_2O solution of DCl.

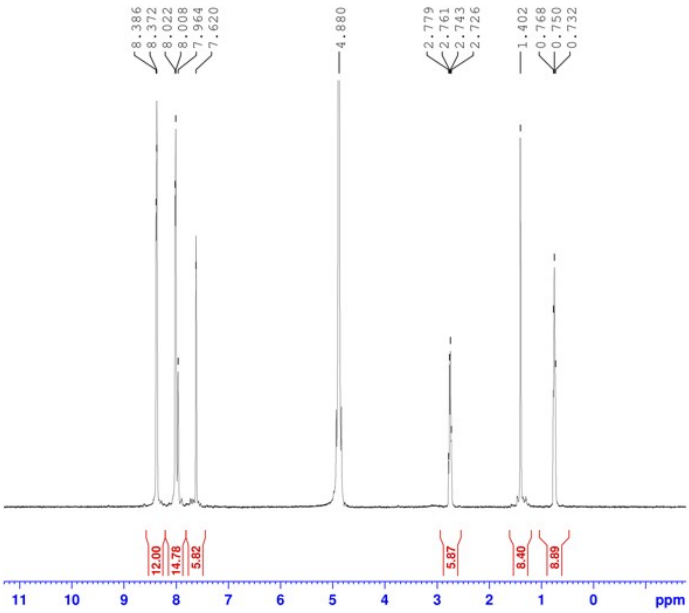

Figure S4. ^{1}H NMR spectrum of **Py^{semi}** in 5 wt% D_2O solution of DCl. The powder sample of **Py^{semi}** was irradiated with UV light for 20 min prior to dissolving into DCl.

5. PXRD

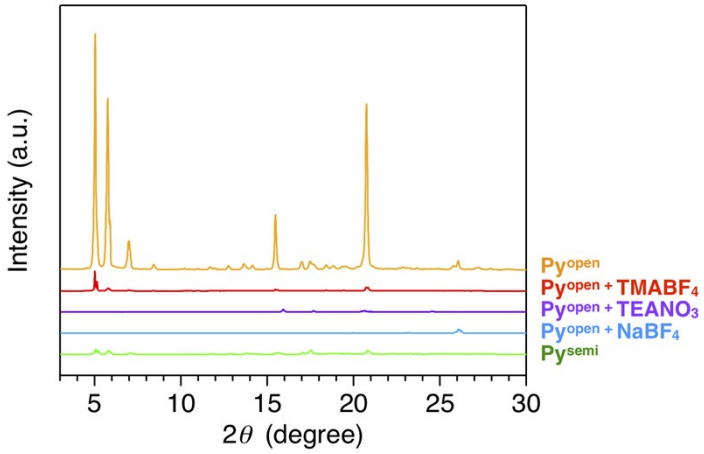

Figure S5. PXRD patterns of **Py^{open}** (orange line), **Py^{semi}** (green line), and **Py^{open}** immersed in aqueous solutions of $TMABF_4$ (red line), $TEANO_3$ (purple line), and $NaBF_4$ (blue line).

6. FT-IR Spectroscopy

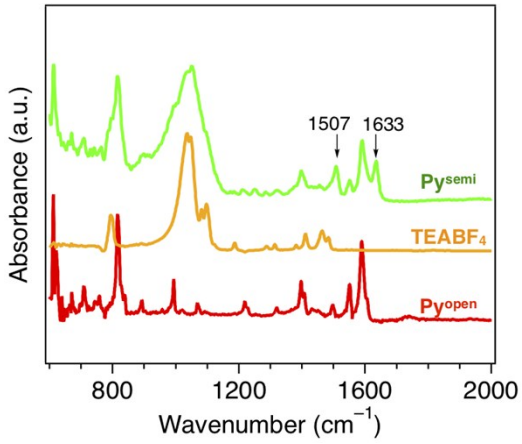

Figure S6. FT-IR spectra of **Py^{semi}** (green line), **Py^{open}** (red line), and $TEABF_4$ (orange line).

7. Electronic Absorption Spectroscopy

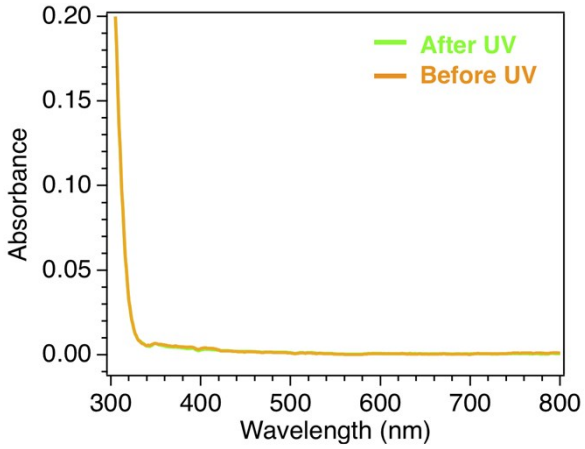

Figure S7. Electronic absorption spectra of acetonitrile solutions containing **Py_6Mes** (100 μM) and $TEABF_4$ (100 μM) before (orange curve) and after (green curve) irradiation of UV light for 3 min.

8. Diffuse Reflectance Spectroscopy

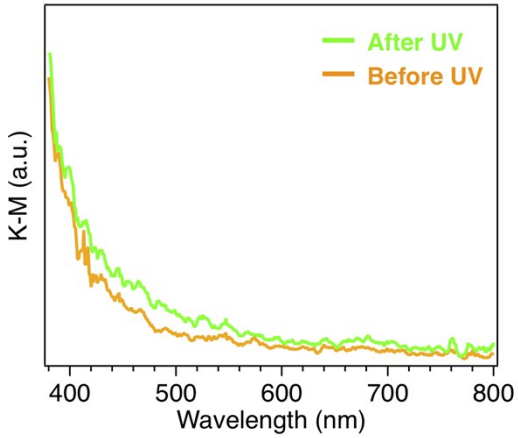

Figure S8. Diffuse reflectance spectra of water-immersed powder samples of **Py^{open}** before (orange curve) and after (green curve) the irradiation with UV light. The powder samples of **Py^{open}** were prepared by immersion into deionized water instead for 24 h at 298K.

9. ESR Spectroscopy

ESR spectra of **Py^{semi}** were recorded on a JEOL RESONANCE JES-FA200 X-band ESR spectrometer. A known amount of powder sample was fixed on a quartz substrate with silicone grease. The quartz substrate was then put in an ESR quartz sample tube and sealed with helium gas. The temperature was controlled with a JEOL RESONANCE ES-CT470 helium gas flow cryostat. The radical concentrations were calibrated with a standard Mn^{2+} marker sample and a solution of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL) as a standard. The UV light irradiation was conducted after cooling down to 20 K.

ESR spectra of **Py^{semi}** after annealing for 1 h at 423 K under constant Ar flow and ESR spectra of **Py^{open}** immersed in aqueous solutions of $NaBF_4$, $TMABF_4$, and $TEANO_3$ were recorded at 100 K on a Bruker model EMXPlus9.5/2.7 equipped with a Bruker N_2-temperature controller. Known among of powder samples were respectively fixed on quartz substrates with silicone grease. The quartz substrates were then put in quartz tubes and sealed after purging with N_2 gas. The 3-min UV light irradiation was conducted after cooling down to 100 K. The *g* values of **Py^{open}** immersed in aqueous solutions of $NaBF_4$, $TMABF_4$, and $TEANO_3$ are 2.00371, 2.00354, and 2.00387, respectively.

10. Supporting Reference

(S1) H. Yamagishi, H. Sato, A. Hori, Y. Sato, R. Matsuda, K. Kato, T. Aida, Self-assembly of lattices with high structural complexity from a geometrically simple molecule. *Science* 2018, **361**, 1242–1246.