Supplementary Information

Formation of Insoluble Perylenetetracarboxylic Diimide Films by Electro- or Photo-Crosslinking of Pyrrole Units

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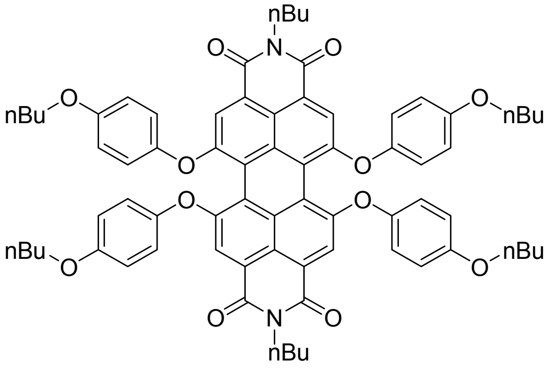
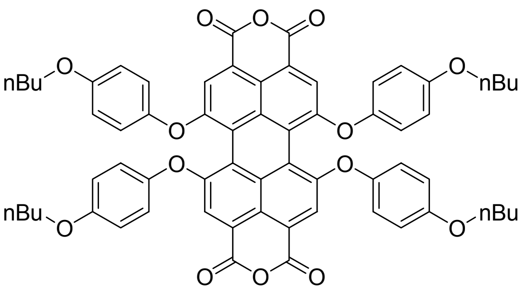
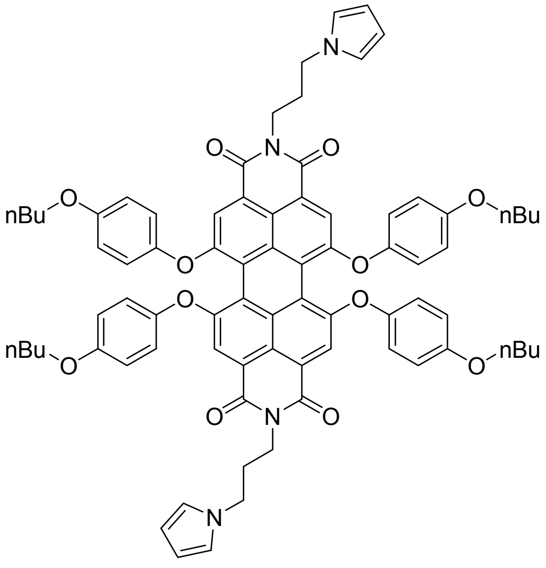
^{1}H-NMR and ^{13}C-NMR spectra were obtained using a Varian Gemini-300 (300 MHz for ^{1}H, and 75 MHz for ^{13}C), or a Varian Inova-500 (500 MHz for ^{1}H, and 125 MHz for ^{13}C) spectrometer. Chemical shifts are reported relative to tetramethylsilane peak (δ 0.00) or solvent peak (δ 7.27 for $CDCl_3$ in ^{1}H NMR, δ 77.2 for $CDCl_3$ in ^{13}C NMR). Elemental analyses were performed by the Organic Chemistry Research Center at Sogang University using a Carlo Erba EA 1180 elemental analyzer. MALDI-TOF was recorded on Voyager-DE STR. IR spectra were obtained using a Thermo-Nicholet Avartar-330 IR spectrometer. THF and ethyl ether were distilled from sodium benzophenone ketyl. Methylene chloride was distilled from calcium hydride. *N,N'*-Bis(*n*-butyl)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid diimide was synthesized in the similar way described in the literature.[i,ii] All other chemicals were used as received otherwise specified.



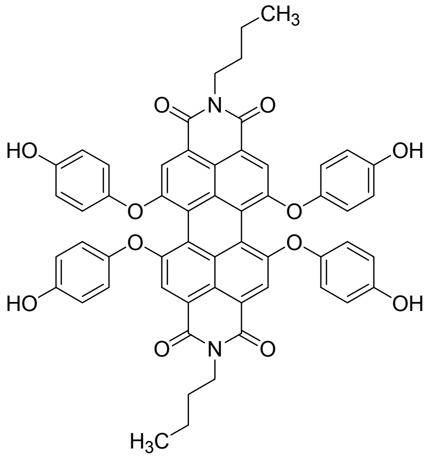
N,N′-Bis(_n_-butyl)-1,6,7,12-tetrakis(4-_n_-butyloxyphenoxy)perylene-3,4,9,10-tetracarboxylic acid diimide (**PDI**): A mixture of compound *N,N′*-Bis(*n*-butyl)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylic acid diimide (6.00 g, 9.37 mmol), 4-butyloxyphenol (9.34 g, 56.2 mmol), K_2CO_3 (7.77 g, 56.2 mmol) in 200 mL of *N*-methyl pyrrolidone (200 mL) was stirred under argon at 160 ^{o}C for 6 h. Hydrochloric acid (2 M, 200 mL) was added to the mixture after cooling to room temperature. The crude precipitates were collected by filtration, washed with water and methanol, and dried under ambient atmosphere. It was purified by flash column chromatography on silica gel with methylene chloride as an eluent to give the desired product as a dark purple solid in 63% (6.81 g, 5.88 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 4H, H_{per}), 6.89 (d, J = 8.5 Hz, 8H, H_{ar}), 6.82 (d, J = 8.5 Hz, 8H, H_{ar}), 4.10 (t, J = 7.5 Hz, 4H), 3.94 (t, J = 6.5 Hz, 8H), 1.77 (m, J = 7.5 Hz, 8H), 1.64 (m, J = 7.5 Hz, 4H), 1.52 (m, J = 8.0 Hz, 8H), 1.39 (m, J = 8.0 Hz, 4H), 1.00 (t, J = 7.0 Hz, 12H, $-CH_3$), 0.93 (t, J = 7.5 Hz, 6H, $-CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.63, 156.85, 156.41, 148.54, 132.99, 122.57, 121.62, 120.00, 119.25, 119.09, 115.95, 68.37, 40.52, 31.52, 30.32, 20.50, 19.44, 14.05, 13.95. Anal. Calcd. for $C_{72}H_{74}N_2O_{12}$: C, 74.59; H, 6.43; N, 2.42. Found: C, 74.46; H, 6.35; N, 2.26. MALDI/TOF-HRMS, calcd. for $C_{72}H_{74}N_2O_{12} + H^+$: 1159.5320, found: 1159.5904.



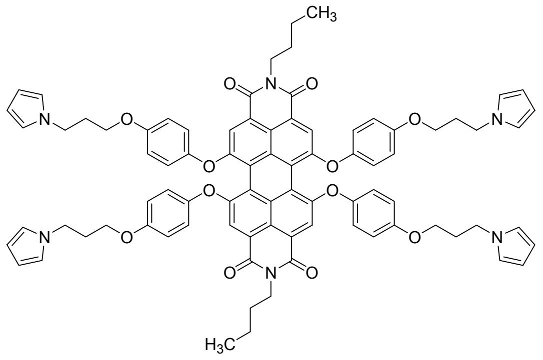
1,6,7,12-tetrakis(4-*n*-butyloxyphenoxy)perylene-3,4,9,10-tetracarboxylic acid dianhydride: A saturated aqueous KOH solution (100 mL) was slowly added to a mixture of **PDI** (5.00 g, 4.31 mmol) in propanol (100 mL). After the color of the mixture turned from violet to green, the mixture was heated at 80 °C and stirred for a day. After cooled to room temperature, the green colored upper layer was separated from the mixture. 35% HCl (aq) was slowly added to the green solution until the pH of the solution became 5 and the resulting mixture was stirred for 8 h. During this procedure, dark red solids precipitated. The red precipites were filtered, washed with water and dried. The red solids were recrystallized in ethyl acetate/hexanes to give the dianhydride a dark purple solid in 84% yield (3.78 g, 3.60 mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 4H, H_{per}), 6.90 (d, J = 8.5 Hz, 8H, H_{ar}), 6.84 (d, J = 9.0 Hz, 8H, H_{ar}), 3.95 (t, J = 6.5 Hz, 8H), 1.79 (m, J = 7.5 Hz, 8H), 1.52 (m, J = 7.5 Hz, 8H), 1.00 (t, J = 7.0 Hz, 12H, $-CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.00, 157.28, 156.85, 147.90, 133.54, 121.63, 121.30, 120.88, 120.58, 118.75, 116.14, 68.41, 31.50, 19.42, 14.04.



***N,N'-Bis*(3-pyrrol-1-yl-propyl)-1,6,7,12-tetrakis(4-*n*-butyloxyphenoxy)perylene-3,4,9,10-tetracarboxylic acid diimide** (**PDI-2Py**): A mixture of 3-pyrrol-1-yl-propylamine (0.1 g, 0.8 mmol) and 1,6,7,12-tetrakis(4-*n*-butyloxyphenoxy)perylene-3,4,9,10-tetracarboxylic acid dianhydride (0.14 g, 0.13 mmol) in 40 mL of H_2O/propanol (1/1 by volume) was stirred at 80 °C for 8 h. After cooled to room temperature, the resulting precipitates were collected by filtration. The precipitates were then purified by flash column chromatography on silica gel with ethyl acetate as an eluent to give **PDI-2Py** a dark purple solid in 86% yield (0.145g, 0.115mmol). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (s, 4H, H_{per}), 6.89 (d, J = 9.0 Hz, 8H, H_{ar}), 6.81 (d, J = 9.0 Hz, 8H, H_{ar}), 6.68 (t, J = 2.0 Hz, 4H), 6.11 (t, J = 2.0 Hz, 4H), 4.11 (t, J = 7.0 Hz, 4H), 3.96 (t, J = 7.0 Mz, 4H), 3.94 (t, J = 6.5 Hz, 8H), 2.17 (qn, J = 7.0 Hz, 4H), 1.78 (m, J = 7.5 Hz, 8H), 1.52 (m, J = 7.5 Hz, 8H), 1.00 (t, J = 7.5 Hz, 12H, $-CH_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.55, 156.88, 156.46, 148.48, 132.99, 122.36, 121.58, 120.60, 120.13, 119.23, 119.18, 115.97, 108.33, 68.38, 47.55, 31.51, 31.10, 29.95, 19.43, 14.04. Anal. Calcd. for $C_{78}H_{76}N_4O_{12}$: C, 74.27; H, 6.07; N, 4.44; O, 15.22. Found: C, 73.32; H, 6.29; N, 4.64. MALDI/TOF-HRMS, calcd. for $C_{78}H_{76}N_4O_{12} + H^+$: 1261.5538, found: 1261.6705.



***N,N'*-Bis-*n*-butyl-1,6,7,12-tetrakis(4-hydroxyphenoxy)perylene-3,4,9,10-tetracarboxylic acid diimide**: BBr_3 (21.8 g, 87.1 mmol) in dry CH_2Cl_2 (20 mL) was added dropwise to a stirred solution of compound **PDI** (6.80 g, 5.86 mmol) in 250 mL of CH_2Cl_2 at room temperature. After stirring for 2 h at room temperature, the solvent was removed by a rotary evaporator. The residue was carefully hydrolyzed by adding ice/water (200 mL) in an ice bath. After adding methanol (100 mL) to the mixture, the resulting mixture was boiled for 1 min. The resulting precipitates were filtered, washed with water/methanol and dried at 80 ^{o}C overnight. The yield was 5.20 g (95%, a dark purple solid): ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.50 (s, 4H, –OH), 7.79 (s, 4H, H_{per}), 6.83 (d, J = 8.5 Hz, 8H, H_{ar}), 6.76 (d, J = 8.5 Hz, 8H, H_{ar}), 3.93 (t, J = 6.5 Hz, 4H), 1.53 (m, J = 7.0 Hz, 4H), 1.29 (m, J = 7.5 Hz, 4H), 0.87 (t, J = 7.5 Hz, 6H, –CH_3). ^{13}C NMR (125MHz, DMSO-d_6) δ 162.54, 156.19, 154.51, 145.56, 132.21, 122.14, 118.48, 118.18, 117.26, 116.36, 114.44, 29.48, 19.68, 13.65. One more peak around 40 ppm was overlapped with the DMSO peak.



***N,N'*-Bis-*n*-butyl-1,6,7,12-tetrakisperylene[4-(3-pyrrole-1-propyloxy)-phenoxy]-3,4,9,10-tetracarboxylic acid diimide** (**PDI-4Py**): A mixture of 3-bromopropylpyrrole (6.06 g, 32.22 mmol), *N,N'*-bis-*n*-butyl-1,6,7,12-tetrakis(4-hydroxyphenoxy)perylene-3,4,9,10-tetracarboxylic acid diimide (5.02 g, 5.37 mmol), CsOH (5.41 g, 32.22mmol), and tetrabutyl ammonium iodide (0.37 g, 1.0 mmol) in 250 mL of DMF was stirred for 10 h. After adding water, the mixture was extracted with methylene chloride and washed with saturated aqueous NaCl solution. The separated organic layer was dried with $MgSO_4$, concentrated, and purified by flash column chromatography on silica gel (CH_2Cl_2/MeOH, 50/1) to give the desired product a dark purple solid (3.30 g, 45%): ^1H NMR (500 MHz, DMSO-d_6) δ 8.11 (s, 4H), 6.83 (d, J = 9.0 Hz, 8H), 6.81 (d, J = 9.0 Hz, 8H), 6.68 (t, J = 2.0 Hz, 8H), 6.17 (t, J = 2.0 Hz, 8H), 4.13 (t, J = 6.5 Hz, 12H), 3.87 (t, J = 6.0 Hz, 8H), 2.12 (m, J = 6.5 Hz, 8H), 1.65 (m, J = 7.5 Hz, 4H), 1.38 (m, J = 7.0 Hz, 4H), 0.93 (t, J = 7.5 Hz, 6H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 163.59, 156.76, 155.94, 148.91, 132.99, 122.65, 121.67, 120.94, 120.07, 119.35, 115.97, 108.44, 64.95, 45.15, 40.55, 31.94, 30.34, 20.50, 13.96. Anal. Calcd. for $C_{84}H_{78}N_6O_{12}$: C, 73.99; H, 5.77; N, 6.16. Found: C, 74.12; H, 5.54; N, 6.07. MALDI/TOF-HRMS, calcd for $C_{84}H_{78}N_6O_{12} + H^+$: 1363.5756, found: 1363.5706.

References

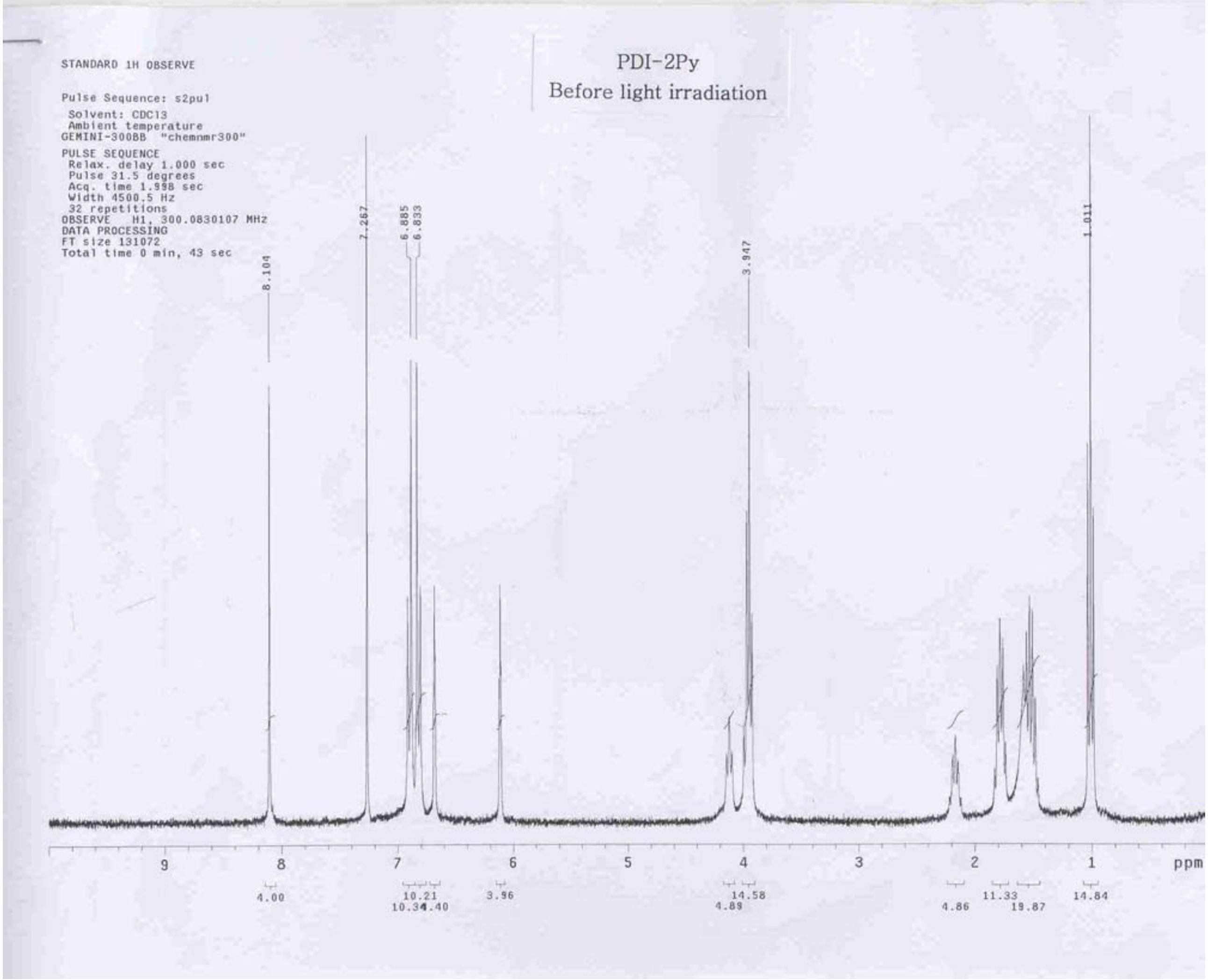
[i] H. Quante, P. Schlichting, U. Rohr, Y. Geerts, K. Müllen, *Macromol. Chem. Phys.* **1996**, *197*, 4029-4044

[ii] C. Former, S. Becker, A. C. Grimsdale, K. Müllen, *Macromolecules* **2002**, *35*, 1576-1582.

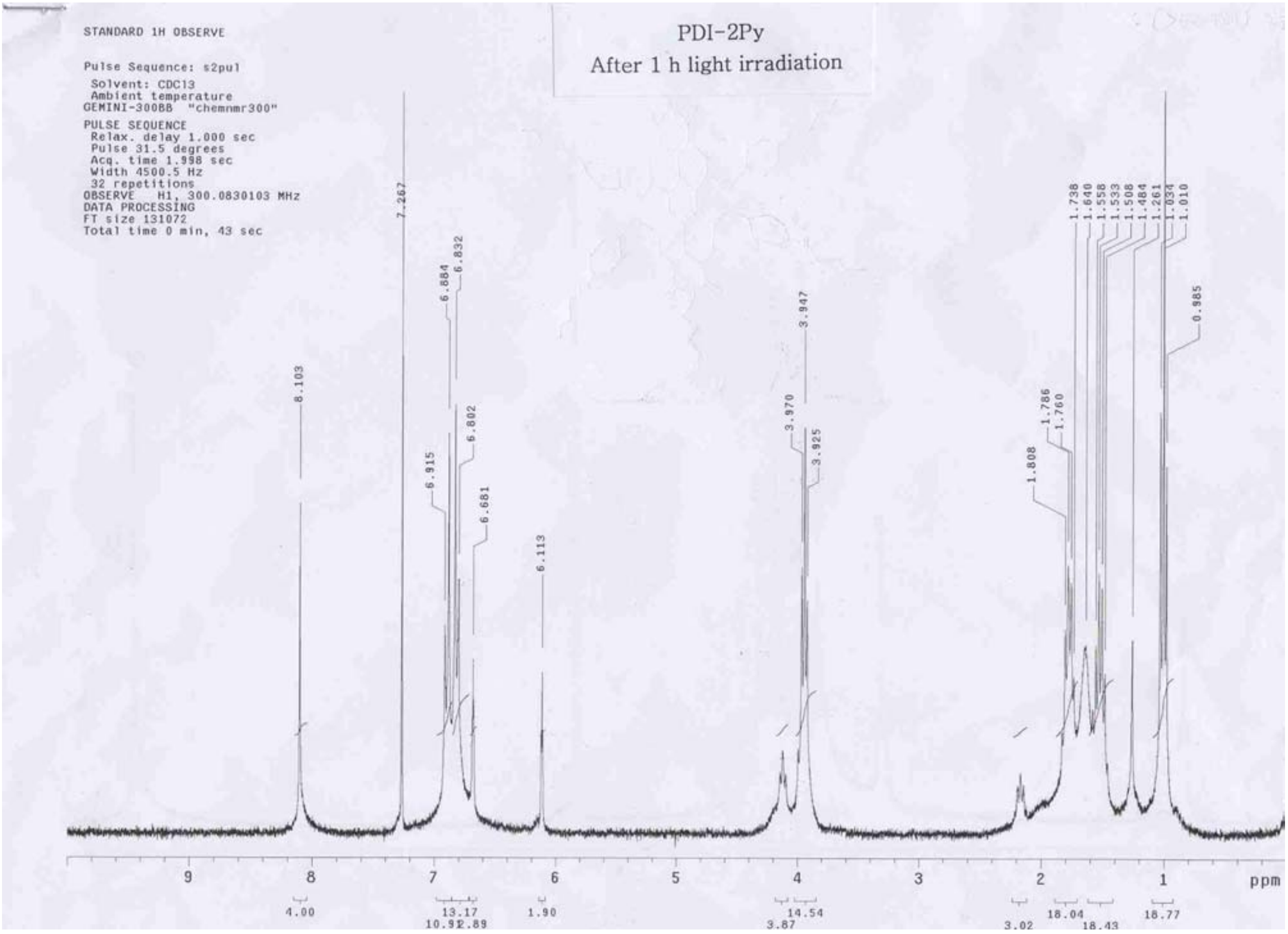
^{1}H-NMR monitoring of the pyrrole coupling reaction of PDI-2Py under visible light irradiation

A solution of **PDI-2Py** in CD_3Cl was placed in an NMR-tube. The NMR tube was irradiated with a Xenon lamp (200 W). A JB510 filter (Zure photonics) and a water chamber were placed between the light source and the NMR tube to cut off the light below 500 nm and to prevent IR caused heating. Progress of the reaction was monitored by ^{1}H-NMR after designated time of irradiation. The spectra obtained are provided below.

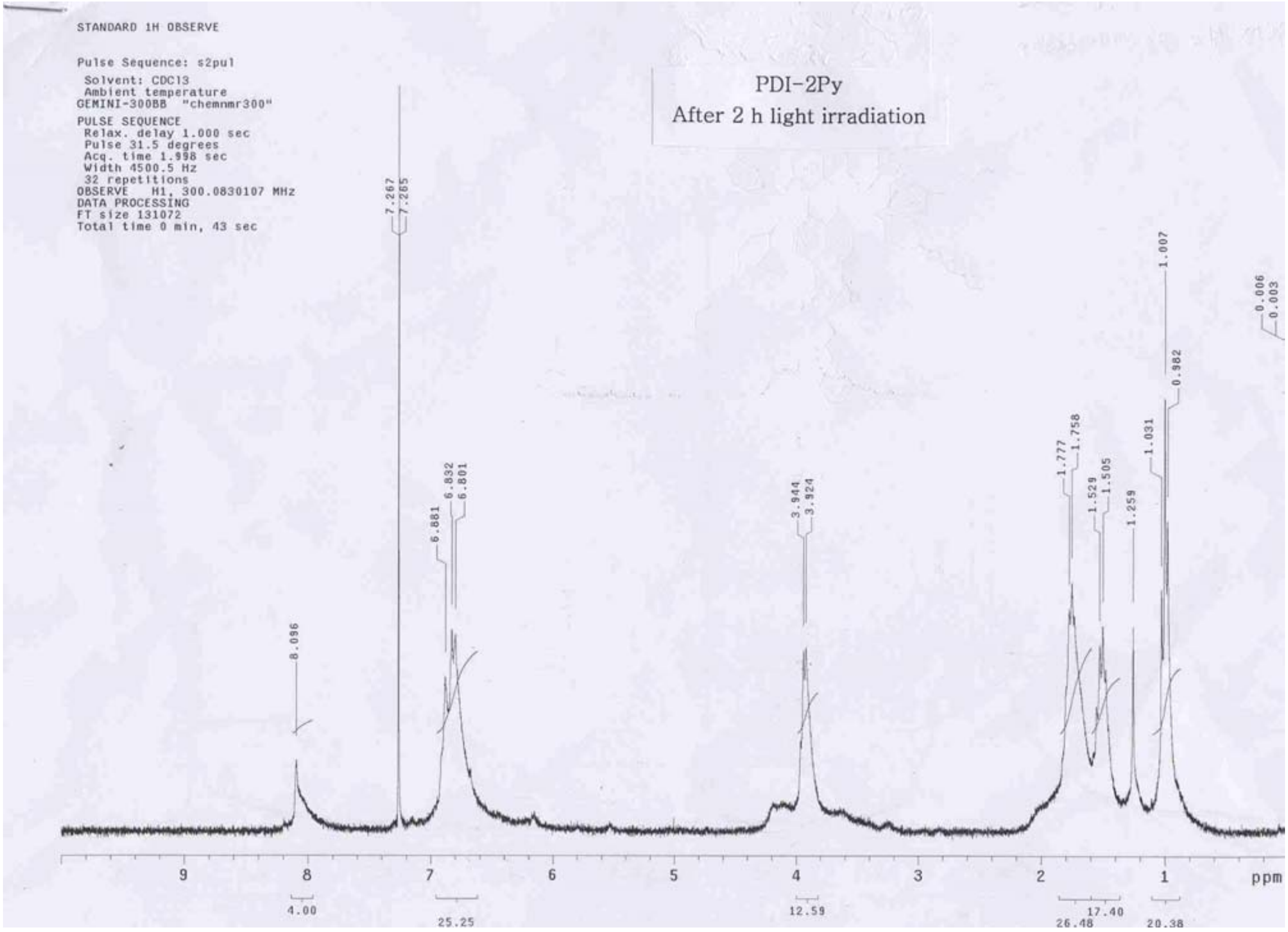
^{1}H-NMR of PDI-2Py (before light irradiation)



^{1}H-NMR of PDI-2Py (after 1 h light irradiation)



^{1}H-NMR of PDI-2Py (after 2 h light irradiation)



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STANDARD 1H OBSERVE

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
GEMINI-300BB  "chemnmr300"
PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 31.5 degrees
 Acq. time 1.998 sec
 Width 4500.5 Hz
 32 repetitions
OBSERVE   H1, 300.0830107 MHz
DATA PROCESSING
FT size 131072
Total time 0 min, 43 sec
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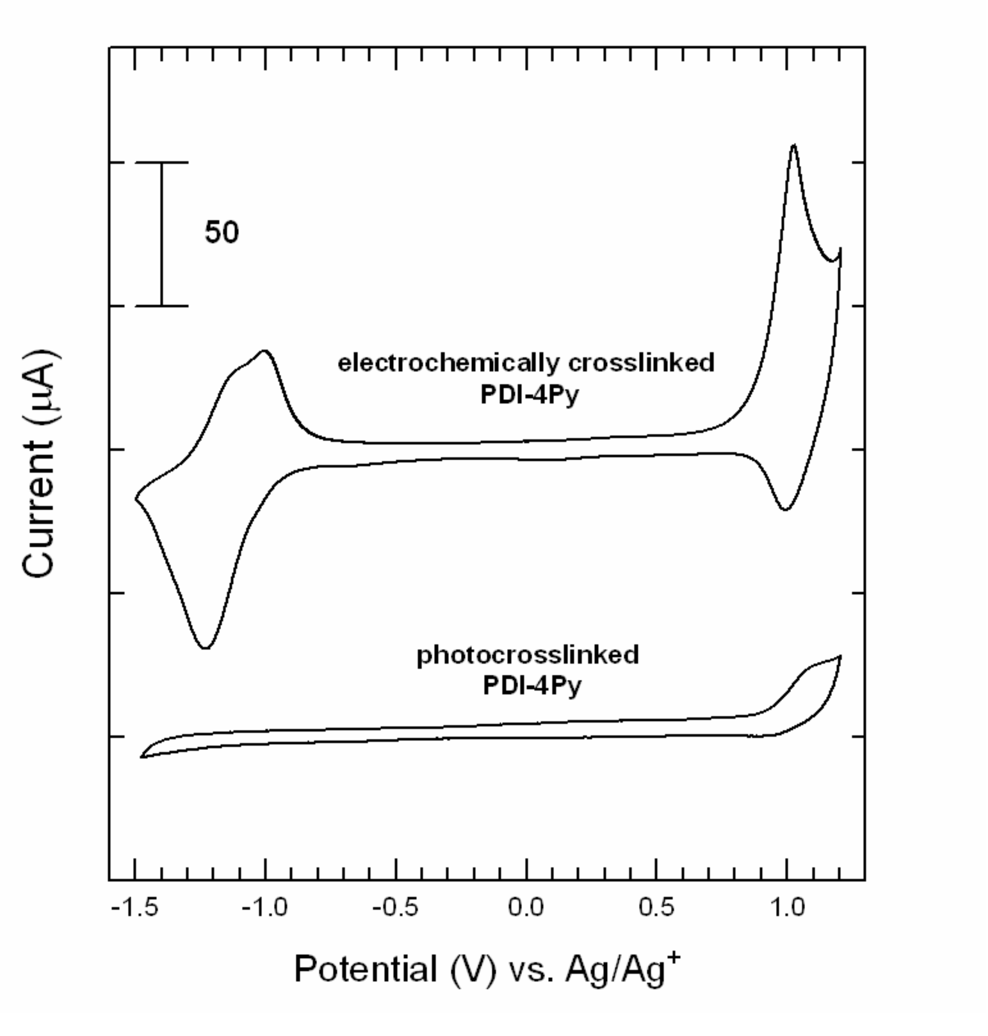
Elemental Analysis (EA) data of a photo-irradiated PDI-2Py film

C: 69.1%, H: 5.4%, N: 2.8%, O: 22.7%

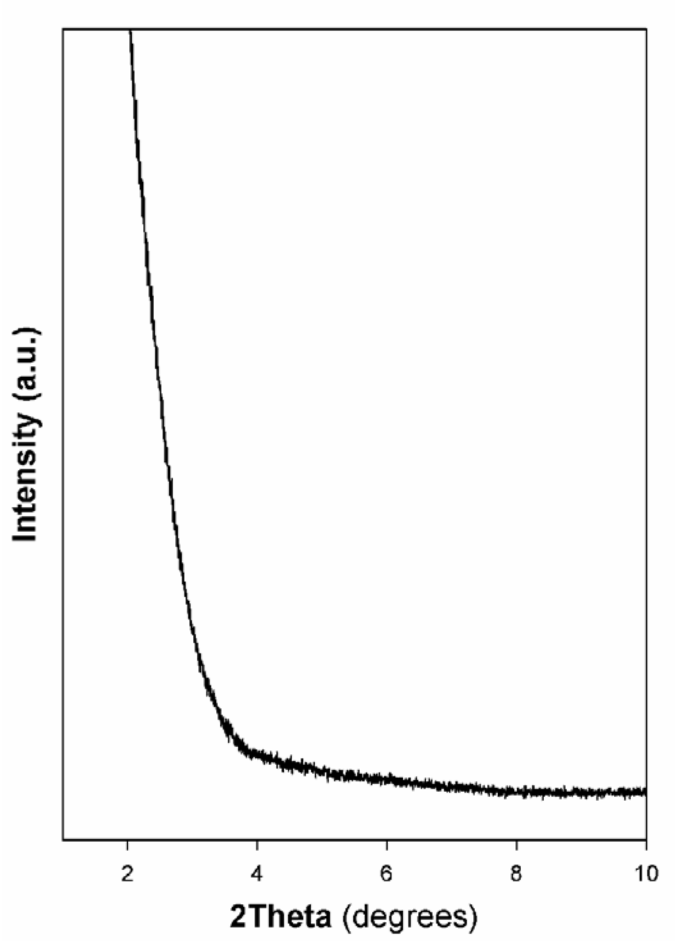
cf) before photo-irradiation: C: 73.3%, H: 6.3%, N: 4.6%, O: 15.8%

Comparison of CV data of an electrochemically crosslinked PDI-4Py film and a photocrosslinked PDI-4Py film

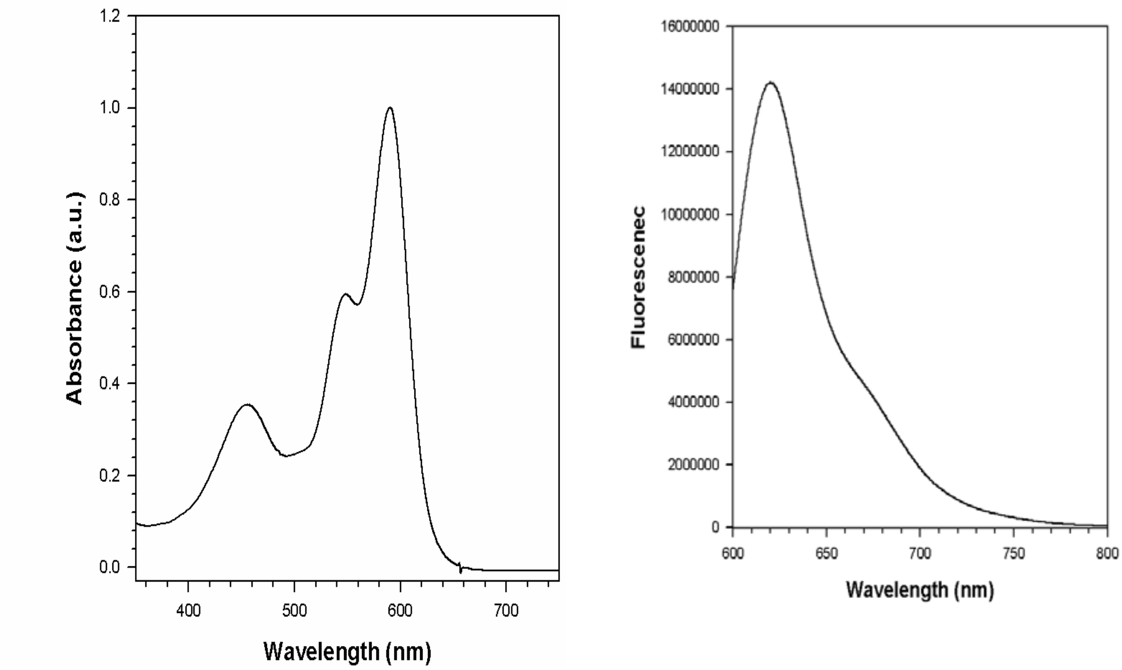


XRD analysis of PDI-4Py Films

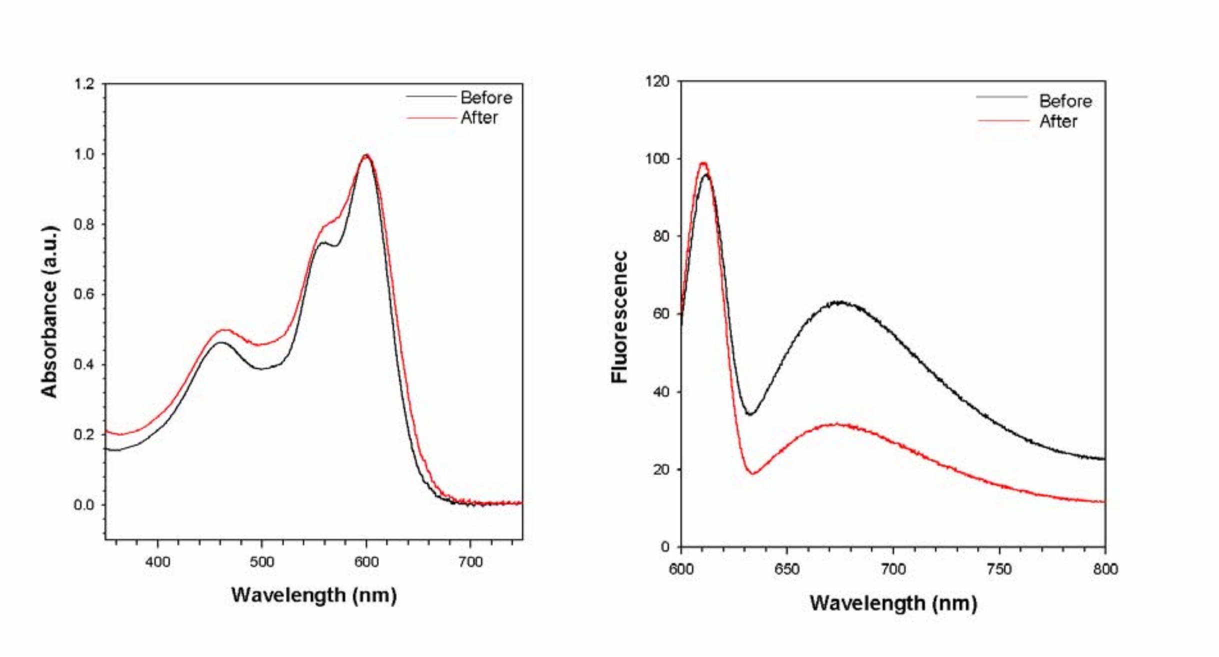
A square shaped glass plate (2.5 cm × 2.5 cm) was spin coated with a solution of **PDI-4Py** solution and the resulting film was exposed to a Xe Lamp filtered below 500 nm for 1 h following the above mentioned experimental set up. The XRD spectrum was obtained using a RIGAKU DMAX 2500 diffractometer in a 2theta/theta mode. No distinguishable peak in this spectrum indicates no significant crystallinity of the film.



UV-Vis and Photoluminescence Spectra of PDI-4Py and PDI-4Py Film



UV-Vis and PL spectra of PDI-4Py monomer solution in $CHCl_3$



UV-Vis and PL spectra of PDI-4Py film before (black) and after (red) photocrosslinking (1 h)