Supporting Information

BAY- AND ORTHO- RING-ANNULATED PERYLENE DIIMIDES: SYNTHESIS AND THEIR PANCHROMATIC ABSORPTION

Ramprasad Regar, Adiki Raja Sekhar, Ruchika Mishra& Jeyaraman Sankar*

Department of Chemistry, Indian Institute of Science Education and Research, Bhopal 462066, Madhya Pradesh, India

E-mail: sankar@iiserb.ac.in*

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Experimental Methods:

Materials and reagents: Spectroscopic grade solvents were used for measuring electrochemical and optical properties. Unless otherwise noted, the chemicals received from Sigma Aldrich were used without further purification. All the reactions were carried out under argon atmosphere. Solvents were dried according to routine procedures. Samples synthesized were purified by column chromatography using silica gel (100-200 mesh) from Merck followed by recrystallisation.

NMR and Mass Spectra Measurements: $^1$H NMR and $^{13}$C NMR spectra were recorded on Bruker Avance 500 MHz spectrometer in CDCl$_3$ at room temperature. The chemical shift values have been referenced to the residual solvent signals. HRMS measurements were recorded on a microTOF-QII high resolution mass spectrometer from Bruker Daltonics coupled to a Waters Acquity UPLC system.

Single Crystal XRD Measurement: Single crystal X-ray diffraction measurements were done on a Bruker Apex diffractometer with a CCD detector with Mo-Kα radiation.

Steady-state absorption and emission measurements: Steady-state absorption spectra were obtained by using UV/VIS/NIR spectrometers (Varian, Cary5000). Silica cell with optical path length of 10 mm was used for all steady-state measurements. Steady-state fluorescence emission measurements were done on a Horiba Jobin Yvon fluorolog 3-111. Quartz cell with optical path length of 10 mm was used for all fluorescence measurements.
Synthetic procedure for precursors:

**PDA:** A mixture of pent-3-ylamine (2.6 mL, 2.2 equiv), perylene-3,4:9,10-tetracarboxylic dianhydride (1 g, 1 equiv) and imidazole (15 g, 60 eq) was stirred at 140°C for 5 h and diluted with ethanol. This was followed by the addition of 2M HCl (100mL). The reaction mixture was then allowed to settle down. The precipitates thus formed were collected through vacuum filtration and dried in oven. Further purification by silica gel chromatography using chloroform as eluent yielded the desired compound (80%).\(^{1}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\)(ppm) = 8.59 (d, \(J = 7.9\) Hz, 4H), 8.53 (d, \(J = 8.0\) Hz, 4H), 5.00 (m, 2H), 2.29 – 2.13 (m, 4H), 1.95 – 1.81 (m, 4H), 0.86 (t, \(J = 7.5\) Hz, 12H).\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\)(ppm) = 158.81, 158.47, 134.49, 129.60, 126.43, 123.01, 77.25, 77.00, 76.75, 57.70, 25.01, 11.34. **APCI HR-MS** mass: Calculated = 531.2278; found= 531.2247.

**PDI-Br:** Excess bromine (4 mL, 86 mmol) was added to a solution of PDI (1 g, 1.3 mmol) in dichloromethane and the reaction mixture was stirred at room temperature for 48 h. The progress of the reaction was monitored by TLC. After the removal of excess bromine, compound was purified by repetitive silica gel column chromatography with hexane/chloroform as eluents. After purification PDI-Br was obtained of yield 57%.\(^{2}\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\)(ppm) = 9.72 (d, \(J = 8.2\) Hz, 1H), 8.85 (s, 1H), 8.63 (dd, \(J = 7.6\) Hz, 3H), 8.55 (dd, \(J = 8.1, 2\)H), 4.99 (m, 2H), 2.19 (m, 4H), 1.93 – 1.82 (m, 4H), 0.86 (m, 12H).\(^{13}\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\)(ppm) = 133.95, 133.59, 129.01, 128.78, 128.18, 128.14, 127.09, 123.78, 123.00, 120.95, 77.25, 77.00,

SII: Synthetic scheme for precursors **PDI**, **PDI-Br** and **PDI-TMS**.
PDI-TMS: A dry Schlenk tube was charged with [Pd (PPh
3
2
2
3
Cl
2
] (4 mol%), CuI (2 mol%), dry THF (5 mL) and N,N-diisopropylamine (5 mL). The resulting solution was degassed vigorously under argon. This was followed by the addition of 1-Bromo -N,N'-Bis(pent-3-yl)perylene-3,4:9,10-tetra-carboxylicbisimide (50 mg, 1 eq) and Trimethylsilyl ethynyl (20 µL, 1.2 eq). The reaction mixture was refluxed at 80°C. The progress of the reaction was monitored by TLC at regular intervals. After the completion of reaction, the solvent was evaporated under vacuum. The reaction mixture was mounted on a column with silica gel (230-400 mesh size) and was eluted with Hexane:Chloroform (20:80). Further purification was done by recrystallisation in hexane/CH2Cl2 to get a red solid of PDI-TMSin excellent yield (95%).

\[ \text{1H NMR} \quad (500 MHz, CDCl}_3 \quad \delta (\text{ppm}) = 10.42 (2d, J=8.26 Hz, 1H), 8.83 (s, 1H), 8.74-8.66 (m, 5H), 5.15-5.04 (m, 2H), 2.35-2.24 (m, 4H), 1.96 (m, 4H), 0.95 (dd, J = 13.9, 7.4 Hz, 12H), 0.44 (s, 9H). \]

\[ \text{13C NMR} \quad (126 MHz, CDCl}_3 \quad \delta (\text{ppm}) = 164.33, 163.95, 162.91, 134.63, 134.54, 134.29, 133.90, 131.07, 129.13, 128.68, 127.22, 127.18, 126.69, 123.48, 123.02, 119.94, 107.23, 105.94, 57.81, 57.73, 36.64, 25.06, 24.99, 24.69, 23.33, 11.35, 11.32. \]

APCI HR-MS mass: calculated = 609.1383; found = 609.1358.
Synthetic procedure for sCDI and pPDI:

**Procedure:** To a solution of compound PDI-TMS (50 mg, 1 equiv) in toluene (5 mL), DBU (250 µL, 20 equiv) was added in a sealed tube. The reaction mixture was then refluxed overnight at 120 °C. After a water work up, the reaction mixture was mounted over a basic alumina column and eluted by chloroform/hexane eluents. The compound was further purified by recrystallisation from a mixture of chloroform and methanol.

**sCDI:** Yield = 22 %. \( ^1H \text{ NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) (ppm) = 9.28 (s, 2H), 9.17 (d, \( J = 8.3 \) Hz, 2H), 8.97 (d, \( J = 8.1 \) Hz, 2H), 8.61 (s, 2H), 5.17 – 5.10 (m, 2H), 2.36 – 2.26 (m, 4H), 2.02 – 1.91 (m, 4H), 0.94 (t, \( J = 7.5 \) Hz, 12H). \( ^{13}C \text{ NMR} \) (126 MHz, CDCl\(_3\)) \( \delta \) (ppm) = 133.09, 130.15, 129.22, 127.25, 124.62, 123.66, 123.03, 57.92, 25.13, 11.43. **APCI HR-MS** mass: calculated = 555.2278; found = 555.2281. **IR** (cm\(^{-1}\)): 3125 (CH stretching mixed with OH), 2091, 1642, 649.

**pPDI:** Yield 14 %. \( ^1H \text{ NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) (ppm) = 8.70 (d, \( J = 8.0 \) Hz, 2H), 8.68 – 8.56 (m, 4H), 8.50 (d, \( J = 8.0 \) Hz, 2H), 7.67 (d, \( J = 3.4 \) Hz, 2H), 7.39 (d, \( J = 3.4 \) Hz, 2H), 5.03 (m, 2H), 4.58 (t, \( J = 6.9 \) Hz, 2H), 3.23 (t, \( J = 6.9 \) Hz, 2H), 3.14 (d, \( J = 9.1 \) Hz, 2H), 2.45 – 2.39 (m, 2H), 2.31 – 2.18 (m, 4H), 1.97 – 1.84 (m, 6H), 1.58 (m, 6H), 0.89 (m, 12H). \( ^{13}C \text{ NMR} \) (126 MHz, CDCl\(_3\)) \( \delta \) (ppm) = 175.94, 140.64, 138.72, 136.00, 135.20, 133.87, 132.21, 129.35, 127.38, 127.01, 126.91, 122.66, 120.83, 103.76, 57.73, 57.56, 49.51, 49.42, 45.71, 37.20, 29.87, 28.55, 28.32, 25.18, 25.05, 23.35, 11.48, 11.35. **APCI HR-MS** mass: calculated = 723.3541; found = 723.3542. **IR** (cm\(^{-1}\)): 3439 (CH stretching mixed with OH), 2091, 1642, 649.
NMR and mass spectra of sCDI and pPDI:

SI3: $^1$H nmr spectra of sCDI.

SI4: $^{13}$C nmr spectra of sCDI.
SI5: COSY nmr spectra of sCDI.

SI6: HSQC nmr spectra of sCDI.
SI7: $^1$H nmr spectra of pPDI.

SI8: $^{13}$C nmr spectra of pPDI.
SI9: COSY nmr spectra of pPDI.

SI10: HSQC nmr spectra of pPDI.
SI11: APCI HR-MS spectra of sCDI.

SI12: APCI HR-MS spectra of pPDI.
SI13: IR of sCDI.

SI14: IR of pPDI.
References:
