SUPPORTING INFORMATION FOR:

Steric Bulk & Solubility Provide Synthetic Access & Insight into Non-Symmetric Perylenediimide Syntheses

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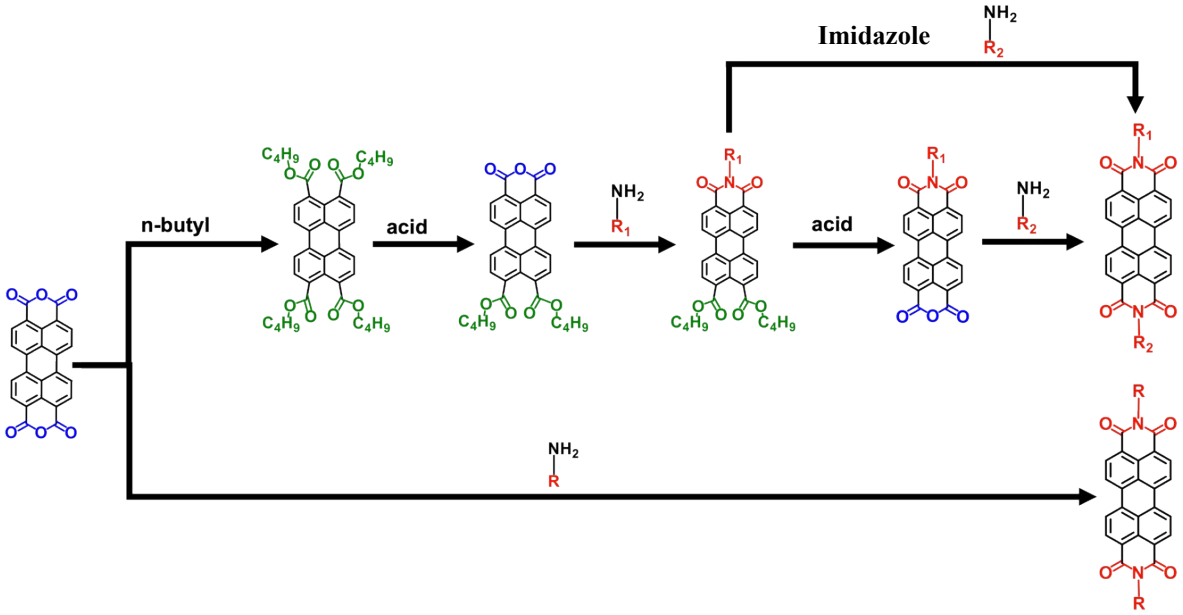


Scheme 1. Synthetic pathways for generating non-symmetric (top portion) or symmetric (bottom portion) PDIs.

Scheme 1 summarizes the general synthetic path and reagents used to produce non-symmetric and symmetric PDIs. Non-symmetric PDIs can be synthesized through five steps where the dianhydride is converted to tetrabutyl ester groups, then selectively converted back to an anhydride. From there, a primary amine was reacted to form the monosubstituted product. Next the other side is converted back to the PMA that can react with a primary amine resulting in a non-symmetric PDI. If the goal is to make a symmetric PDI that can be achieved in a single step where the primary amine is reacted with the dianhydride starting material.

General Methods

Materials:

Perylene-3,4,9,10-tetracarboxylic acid, n-bromobutanol, 1,8-diazabicyclo [5.4.0] undec-7-ene, were purchased from TCI and used as received. Zinc acetate dihydrate, imidazole were purchased from Acros organics. NMP and common solvents were purchased from Fisher. P-Toluenesulfonic acid monohydrate and amines were purchased form Sigma Aldrich. All reagents were used as received.

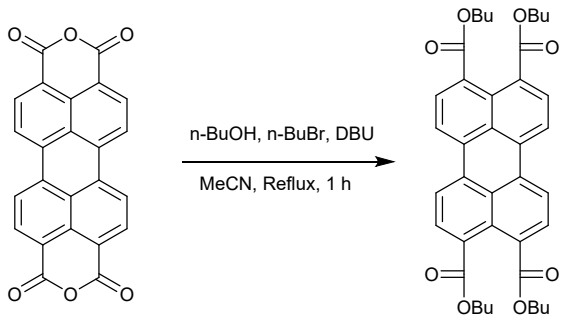
LCMS

Mass spectra were taken using Agilent Technologies 6125B Single Quadrupole LC/MS using CI.

NMR:

To increase NMR quality, each compound was assessed for solubility in toluene, acetonitrile, acetone, DMSO, THF, chloroform, and if necessary benzene to find the highest solubility for the collected spectra. In typical fashion for perylene diimide synthesis, proton, and fluorine NMR were used as primary methods of characterization, as their abundance is sufficiently high to detect low concentrations, while concentrations required to detect ^{13}C NMR is much greater. It is well established in literature that carbon NMR is not an apt method of characterization for these molecules. Instead, mass spectra, ^{1}H NMR, and ^{19}F NMR were employed to characterize these novel compounds to the standard of the PDI field, though the y-axis was carefully included, as many proton NMRs that are displayed do not include this critical reference.[1–6] It is also uncommon to find displayed proton spectra, as most articles simply list NMR value which obscures the challenging nature of PDI ^{1}H NMR. It is for this reason that these NMRs were specifically displayed in the supporting information to help contextualize the solubility issues of these compounds. NMR were taken with a Bruker instrument equipped with a 400 MHz OneNMR 5 mm probe at room temperature.

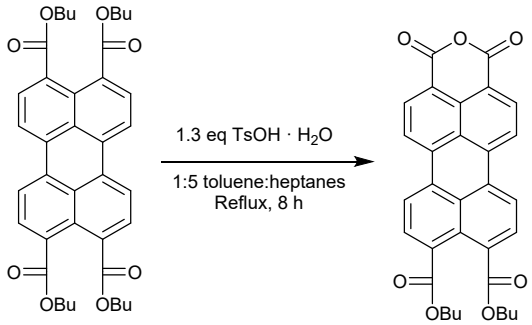
2. Non-symmetric Procedures



Scheme 2.1 Reaction scheme for converting the dianhydride to the symmetric tetrabutyl ester derivative.

An amount of perylene-3,4,9,10-tetracarboxylic dianhydride (5.14 g, 2.5 mmol) was suspended in 25 mL of MeCN, *n*-bromobutane (20 mL, 185 mmol), *n*-butanol (19.4 mL, 212 mmol), and 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU:17.8 mL, 119 mmol). The suspension was sonicated for 20 min to help with mixing. The reaction mixture was stirred and refluxed at 90 °C for 1 hour. The resultant orange precipitate was collected via vacuum filtration and rinsed with MeCN, ethanol, and water. (Standard method) Average yield: 8.22 g (96%). ^{1}H NMR (400 MHz, CDCl3, 25 °C):

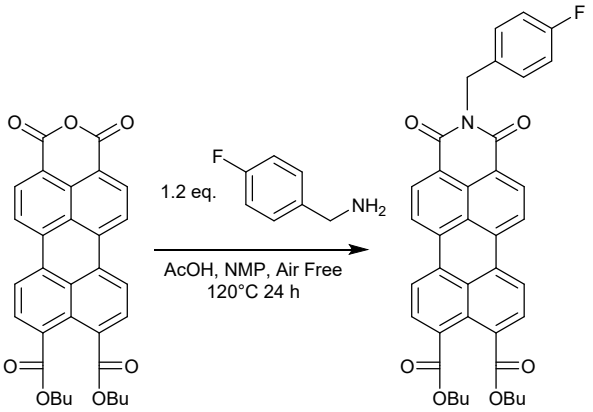
δ 8.23 (d, *J* = 8.0 Hz, 4H), 8.04 – 7.97 (m, 4H), 4.33 (t, *J* = 6.9 Hz, 8H), 1.77 (p, *J* = 7.1 Hz, 8H), 1.48 (m, *J* = 7.4 Hz, 8H), 1.03 – 0.94 (m, 12H).Exact MS (-CI): *m/z* calculated for $C_{40}H_{44}O_8$, 652.30 *m/z*; observed 652.33. *m/z.* IR solid state (ν, cm^{-1}): 2956 (m), 2870 (m), 2863 (m), 1720 (s), 1706 (s), 1587 (s), 1469 (w), 1263 (s), 1164 (s), 1128 (m), 1093 (m), 936 (w), 841 (m), 802 (m), 744 (w).



Scheme 2.2

Reaction scheme for converting the symmetric tetrabutyl ester derivative to non-symmetric PMA.

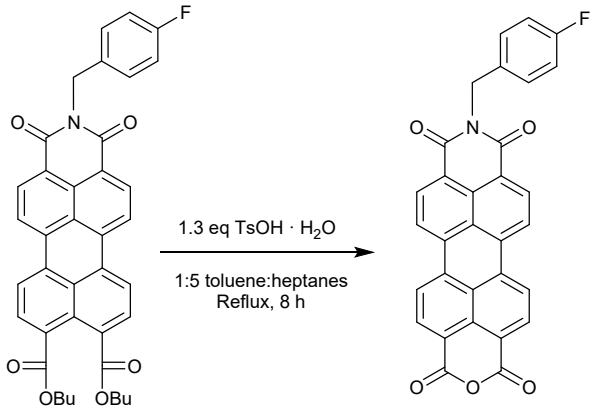
Tetrabutylester perylene 3,4,9,10-tetracarboxylic acid (8.22 g, 12.6 mmol) was suspended in 250 mL of a 1:5 toluene:*n*-heptane mixture. The slurry was sonicated for 20 minutes. The *p*-toluenesulfonic acid (3.11 g, 16.4 mmol) was added to the reaction mixture and was then refluxed at 120 °C for 6 hours. The resulting mixture was cooled to room temperature, and the 1:5 toluene:*n*-heptane was removed by vacuum filtration. The resulting red precipitate was washed with three aliquots of each solvent *n*-hexane, acetonitrile, and methanol to remove any unreacted starting product and residual solvent. The solid was further washed with $CHCl_3$ in a Soxhlet extraction to remove remaining impurities. The red-orange reaction precipitate was collected as the desired product. (Standard method) Average yield: 5.86 g (88%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ 8.66 (d, *J* = 7.9 Hz, 2H), 8.54 (dd, *J* = 10.8, 7.9 Hz, 4H), 8.15 (d, *J* = 7.7 Hz, 2H), 4.35 (t, *J* = 6.8 Hz, 4H), 1.79 (q, *J* = 7.3 Hz, 4H), 0.99 (t, *J* = 7.4 Hz, 6H). Exact MS (-CI): *m/z* calculated for $C_{32}H_{26}O_7$, 522.17 *m/z*; observed 521.29 *m/z*. IR solid state (ν, cm^{-1}): 2951 (m), 2877 (m), 1771 (s), 1720 (s), 1696 (s), 1591 (s), 1509 (s), 1268 (s), 1254 (s), 1147 (m), 1115 (m), 1124 (m), 1008 (m), 805 (s), 737 (s).



Scheme 2.3 Reaction scheme for converting the non-symmetric PMA derivative to the 4-fluorobenzylamine-imide dibutylester derivative.

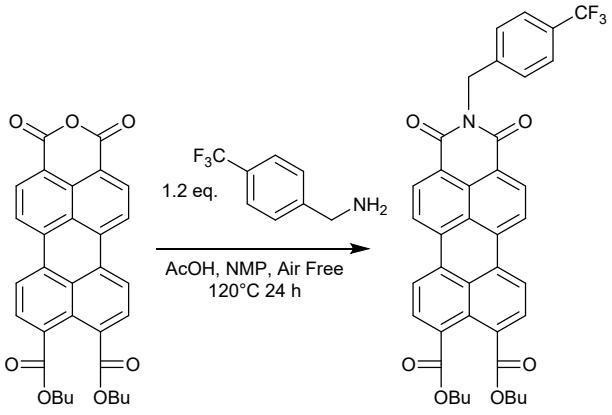
A solution of monoandyhride dibutylester perylene 3,4,9,10-tetracarboxylic (1.11 g, 1.94 mmol), 50 mL of *N*-methyl-2-pyrrolidone (NMP), glacial acetic acid (0.8 mL, 10.3 mmol), and 4-fluorobenzylamine (0.25 mL, 2.10 mmol) was prepared. The reaction mixture was stirred under N_2 and heated 120 °C for 24 hours. The resulting mixture was cooled to room temperature and poured into water, yielding a precipitate that was isolated via vacuum filtration. The red precipitate was washed with several aliquots of water to remove any residual NMP. The red reaction precipitate was collected as the desired product. (known methods for a novel product) Average yield: 0.962 g (64%). ^{1}H NMR (400 MHz, CDCl3, 25 °C): δ 8.67 – 8.60 (m, 2H), 8.55 – 8.46 (m, 4H), 8.16 – 8.09 (m, 2H), 7.58 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 4.34 (dt, *J* = 7.1, 3.8 Hz, 4H), 1.83 – 1.73 (m, 4H), 1.56 – 1.43 (m, 3H), 1.00 (dt, *J* = 10.2, 5.1 Hz, 6H) ^{19}F NMR (376 MHz, CDCl3, 25 °C): *δ* -114.78 (s 1F). Exact MS (-CI): *m/z* calculated for $C_{39}H_{32}FNO_6$, 629.22 *m/z*;

observed 629.21 *m/z*. IR solid state (ν, cm^{-1}): 2951 (m), 2877 (m), 1771 (s), 1696 (s), 1720 (s), 1591 (s), 1509 (s), 1268 (s), 1254 (s), 1147 (m), 1115 (m), 1124 (m), 1008 (m), 805 (s), 737 (s).



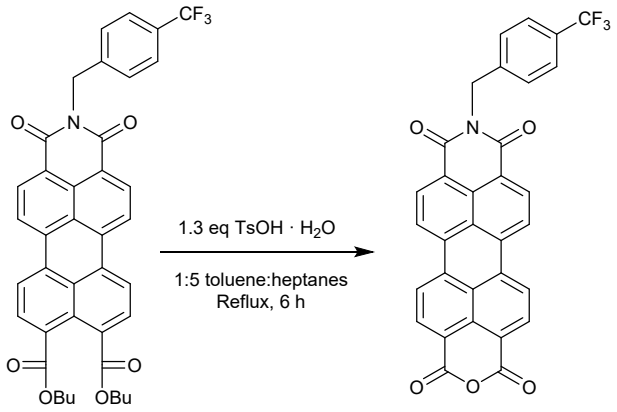
Scheme 2.4 Reaction scheme for converting the 4-fluorobenzylamine monoimide dibutylester derivative to the 4-fluorobenzyl-imide monoanhydride derivative.

An amount 4-Fluorobenzyl-imide dibutylester perylene 3,4,9,10-tetracarboxylic acid (1.08 g, 1.60 mmol) was suspended in 60 mL of a 1:5 toluene:*n*-heptane mixture. The slurry was sonicated for 20 minutes. The *p*-toluenesulfonic acid (0.850 g, 4.4 mmol) was added to the reaction mixture, which was then refluxed at 120 °C for 8 hours. The resulting mixture was cooled to room temperature, and the 1:5 toluene:*n*-heptane was removed by vacuum filtration. The resulting maroon precipitate was washed with three aliquots of each solvent *n*-hexane, acetonitrile, chloroform, and water to remove any unreacted starting product and residual solvent. (Known method for novel product) Average yield: 0.817 g (93%). Product was not soluble enough to obtain a ^{1}H NMR spectrum. Exact MS (-CI): *m/z* calculated for $C_{31}H_{14}FNO_5$, 499.08 *m/z*; observed 499.08 *m/z*. IR solid state (ν, cm^{-1}): 2959 (m), 2870 (m), 1768 (s), 1737 (s), 1689 (m), 1653 (m), 1586 (m), 1509 (s), 1402 (s), 1300 (m), 1159 (m), 1117 (m), 1006 (m), 808(s), 733 (s), 549 (m).



Scheme 2.5 Reaction scheme for converting the non-symmetric monoandyhride dibutylester derivative to the 4-(trifluoromethyl)benzyl-imide monobutylester derivative.

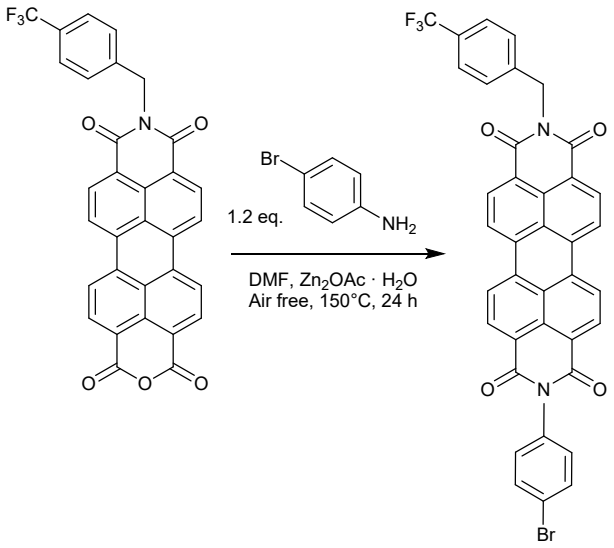
A solution of monoandyhride dibutylester perylene 3,4,9,10-tetracarboxylic acid (1.01 g, 1.92 mmol), 20 mL of *N*-methyl-2-pyrrolidone (NMP), glacial acetic acid (0.8 mL, 10.3 mmol), and 4-(trifluoromethyl) benzylamine (0.3 mL, 2.13 mmol) was prepared. The reaction mixture was stirred under N_2 and heated 120 °C for 24 hours. The resulting mixture was cooled to room temperature and poured into water, yielding a precipitate that was isolated via Büchner funnel vacuum filtration. The red precipitate was washed with several aliquots of water to remove any residual NMP. The red precipitate was collected as the desired product. (Known method for novel product) Average yield: 1.13 g (83%). ^{1}H NMR (400 MHz, CDCl3, 25 °C): δ 8.64 (dd, *J* = 8.0, 1.7 Hz, 2H), 8.48 (t, *J* = 8.7 Hz, 4H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 5.44 (s, 2H), 4.38 – 4.30 (m, 4H), 1.78 (m, *J* = 6.6 Hz, 4H), 1.53 – 1.43 (m, 4H), 0.99 (td, *J* = 7.4, 2.0 Hz, 6H).. ^{19}F NMR (376 MHz, CDCl3, 25 °C): *δ* -62.67 (s 3F). Exact MS (-CI): *m/z* calculated for $C_{40}H_{32}F_3NO_6$, 679.22 *m/z*; observed 679.23 *m/z.* IR solid state (ν, cm $^{-1}$): 2956 (m), 2781 (m), 1720 (s), 1703 (s), 1595 (s), 1540 (m), 1256 (s), 1244 (s), 1117 (m), 1110 (m), 1125(m), 1001 (m), 803 (s), 756(s).



Scheme 2.6 Reaction scheme for converting non-symmetric the 4-(trifluoromethyl)benzyl-imide dibutylester derivative to the 4-(trifluoromethyl)benzyl-imide monoanhydride derivative.

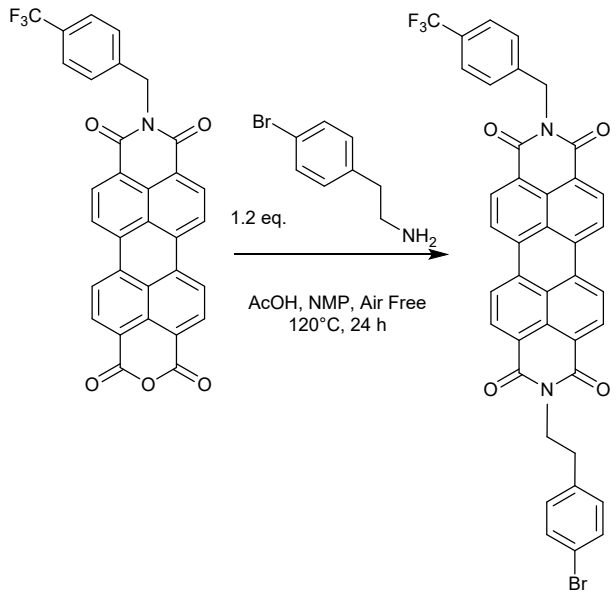
An amount 4-(Trifluoromethyl)benzyl-imide dibutylester perylene 3,4,9,10-tetracarboxylic acid (1.07 g, 1.47 mmol) was suspended in 60 mL of 1:5 toluene:*n*-heptane mixture. The slurry was sonicated for 20 minutes. The *p*-toluenesulfonic acid (0.784 g, 4.20 mmol) was added to the reaction mixture which was then refluxed at 120 °C for 8 hours. The resulting mixture was cooled to room temperature and the 1:5 toluene:*n*-heptane was removed via vacuum filtration. The resulting maroon precipitate was washed with three aliquots of each solvent *n*-hexane, acetonitrile, chloroform, and water to remove any unreacted starting product and residual solvent. (Known method for a novel product) Average yield: 0.862 g (96%). Product was not soluble enough to obtain a ^{1}H NMR spectrum. Exact MS (-CI):

m/z calculated for $C_{32}H_{14}F_3NO_5$, 549.08 *m/z*; observed 549.08. *m/z* IR solid state (ν, cm^{-1}): 2989 (m), 2880 (m), 1758 (s), 1727 (s), 1672 (m), 1633 (m), 1580 (m), 1512 (s), 1350 (m), 1169 (m), 1120 (m), 1001 (m), 803(s), 756 (s), 548 (m).



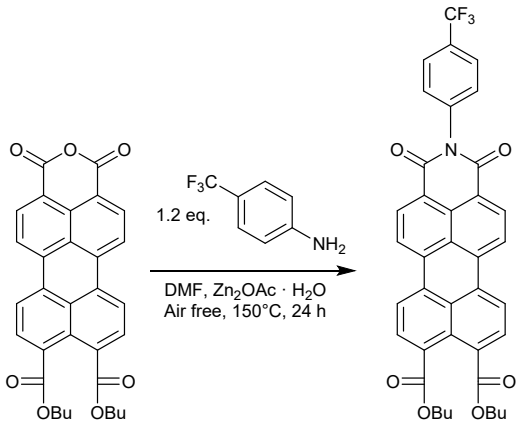
Scheme 2.7 Reaction scheme for converting the 4-(trifluoromethyl)benzyl-imide monoanhydride derivative to the non-symmetric 4-bromoaniline-imide derivative.

An amount of 4-(Trifluoromethyl)benzyl-imide monoanhydride perylene 3,4,9,10-tetracarboxylic acid(0.471 g, 0.858 mmol), 20 mL of dimethylformamide (DMF), zinc acetate monohydrate (0.091 g, 0.414 mmol), and 4-bromoaniline (0.345 g, 2.12 mmol) were combined. The reaction mixture was stirred under N_2 and heated 150 °C for 24 hours. The resulting mixture was cooled to room temperature, ice cold water was added to precipitate the reaction, and the slurry was separated via vacuum filtration. The resulting dark red precipitate was washed with ethanol, methanol, and water to remove any residual DMF and aniline material. The dark red precipitate was collected as the desired product. (Known method for novel product) Average yield: 0.454 g (75%). ^{1}H NMR (400 MHz, CDCl3, 25 °C): δ 8.72 (d, *J* = 7.9 Hz, 8H), 7.69 (d, *J* = 13.6 Hz, 4H), 7.58 (m, 4H), 5.44 (d, *J* = 6.5 Hz, 2H).^{19}F NMR (376 MHz, CDCl3, 25 °C): *δ* -62.67 (s 3F). Exact MS (-Cl): *m/z* calculated for $C_{38}H_{18}BrF_3N_2O_4$, 702.04 *m/z*; observed 702.12 *m/z* IR solid state (ν, cm^{-1}): 1711 (s), 1704 (s), 1635 (s), 1590 (m), 1565 (m), 1246 (s), 1243 (s), 1127 (m), 1120 (m), 1111(m), 1001 (m), 834 (s), 756(s), 597 (m).



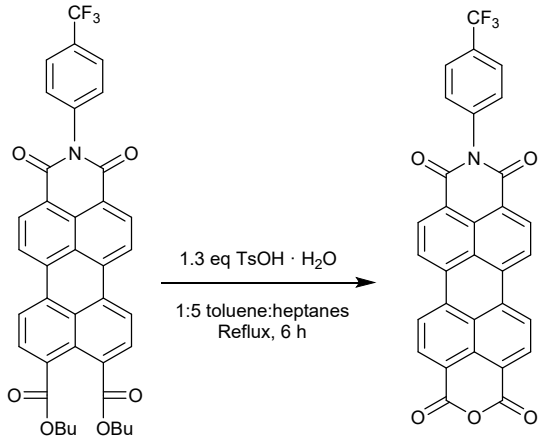
Scheme 2.8 Reaction scheme for converting the 4-(trifluoromethyl)benzyl-imide monoanhydride derivative to the non-symmetric 4-bromophenylethylamine-imide derivative.

An amount of 4-(Trifluoromethyl)benzyl-imide monoanhydride perylene 3,4,9,10-tetracarboxylic (0.5 g, 0.91 mmol), 60 mL of *N*-methyl-2-pyrrolidone (NMP), glacial acetic acid (0.8 mL, 010.3 mol), and 4-bromophenylethylamine (0.3 mL, 1.99 mmol) were combined. The reaction mixture was stirred under N_2 and heated 120 °C for 24 hours. The resulting mixture was cooled to room temperature, poured into water, and the resulting precipitate was isolated via vacuum filtration. The brown precipitate was washed with several aliquots of water to remove any residual NMP. The brown reaction precipitate was collected as the desired product. (Known methods for novel product) Average yield: 0.655 g (98%). ^{1}H NMR (400 MHz, CDCl3, 25 °C): δ 8.74 (m, 4H), 8.49 (d, 2H), 7.51 (m, 6H), 7.40 (m 4H), 5.4 (s 2H), 4.34 (t, 2H), 3.00 (t, 2H). ^{19}F NMR (376 MHz, CDCl3, 25 °C): δ -62.67 (s 3F).Exact MS (-CI): *m/z* calculated for $C_{40}H_{22}BrF_3N_2O_4$, 730.07 *m/z*; observed 730.17 *m/z*. IR solid state (ν, cm^{-1}): 2953 (m), 2761 (m), 1710 (s), 1701 (s), 1601 (s), 1640 (m), 1257 (s), 1243 (s), 1119 (m), 1109 (w), 1121 (w), 1001 (m), 811 (s), 757(s).



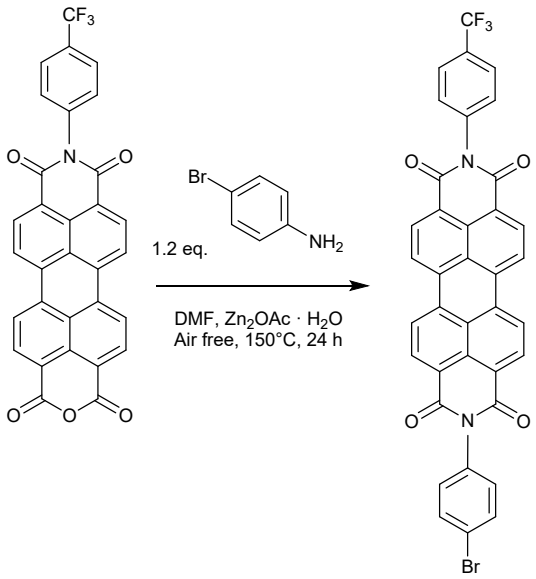
Scheme 2.9 Reaction scheme for converting the non-symmetric PMA derivative to the non-symmetric 4-trifluoromethyl aniline-imide dibutylester derivative.

An amount of monoandyhride dibutylester perylene 3,4,9,10-tetracarboxylic acid (0.252 g, 0.483 mmol), 20 mL of dimethylformamide (DMF), zinc acetate monohydrate (0.047 g, 0.21 mmol), and 4-trifluroromethylaniline (0.08 g, 0.64 mmol) were combined. The reaction mixture was stirred under N_2 and heated to 150 °C for 24 hours. The resulting mixture was cooled to room temperature, ice cold water was added to precipitate the reaction, and the slurry was separated via vacuum filtration. The resulting dark red was washed with ethanol, methanol, and water to remove any residual DMF and aniline material. The dark red powder was collected as the desired product. (Known method for known product) Average yield: 0.268 g (83%). ^{1}H NMR (400 MHz, CDCl3, 25 °C): δ 8.71 – 8.59 (m, 2H), 8.53 – 8.45 (m, 4H), 8.12 (dd, *J* = 7.7, 2.4 Hz, 2H), 7.75 (d, *J*=7.3 2H), 4.35 (t, *J* = 6.7 Hz, 4H), 1.83 – 1.75 (m, 4H), 1.48 (t, *J* = 7.5 Hz, 4H), 1.00 (dt, *J* = 7.5, 3.7 Hz, 6H). ^{19}F NMR (376 MHz, CDCl3, 25 °C): *δ* -62.67 (s 3F). Exact MS (-CI): *m/z* calculated for $C_{39}H_{30}F_3NO_6$, 665.20 *m/z*; observed 665.19 *m/z.* IR solid state (ν, cm^{-1}): 2958 (m), 2783 (m), 1722 (s), 1713 (s), 1597 (s), 1543 (w), 1258 (s), 1234 (s), 1114 (m), 1125(m), 1115 (m), 967 (s), 801 (s), 743 (s).



Scheme 2.10 Reaction scheme for converting the non-symmetric 4-trifluoromethyl aniline-imide dibutylester derivative to the 4-trifluoromethyl aniline monoanhydride derivative.

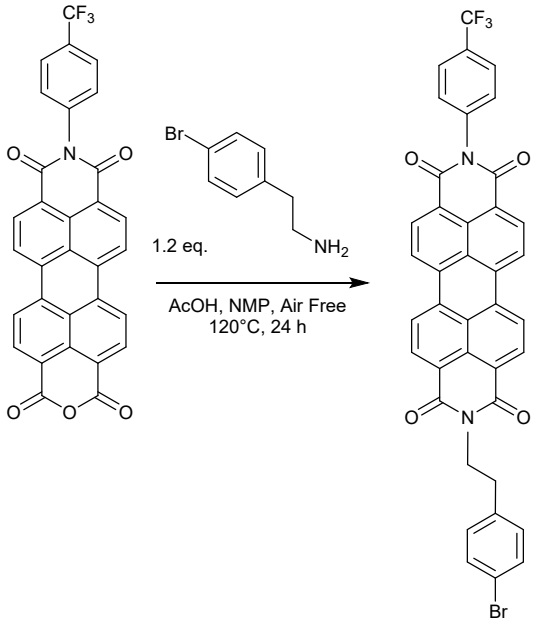
An amount of 4-Trifluoromethyl aniline-imide dibutylester perylene 3,4,9,10-tetracarboxylic acid (0.104 g, 0.156 mmol) was suspended in 60 mL of 1:5 toluene:*n*-heptane mixture. The slurry was sonicated for 20 minutes. The *p*-toluenesulfonic acid (0.209 g, 1.09 mmol) was added to the reaction mixture and was then refluxed at 120 °C for 20 hours. The resulting mixture was cooled to room temperature and the 1:5 toluene:*n*-heptane was removed by vacuum filtration. The resulting dark red precipitate was washed with three aliquots of each solvent *n*-hexane, acetonitrile, chloroform, and water to remove any unreacted starting product and residual solvent. (Known method for known product) Average yield: 0.048 g (57%). ^{1}H NMR (400 MHz, CDCl3, 25 °C): δ 9.03 (s, 8H), 7.77 (d, *J* = 7.9 Hz, 4H), ^{19}F NMR (376 MHz, CDCl3, 25 °C): *δ* -62.67 (s 3F). Exact MS (-CI): *m/z* calculated for $C_{31}H_{12}F_3NO_5$, 535.07 *m/z*; observed 549.06. *m/z.* IR solid state (ν, cm^{-1}): 2986 (m), 2881 (m), 1756 (s), 1725 (s), 1671 (m), 1632 (m), 1584 (m), 1515 (s), 1352 (m), 1171 (m), 1122 (m), 1007 (m), 809(s), 751 (s), 538 (m), 527 (m).



Scheme 2.11 Reaction scheme for converting the 4-trifluoromethyl aniline monoanhydride derivative to non-symmetric the 4-bromoaniline-imide derivative.

An amount of 4-Trifluoromethyl aniline monoanhydride perylene 3,4,9,10-tetracarboxylic acid (0.554 g, 0.93 mmol), 20 mL of dimethylformamide (DMF), zinc acetate monohydrate (0.091 g, 0.414 mmol), and 4-bromoaniline (0.391 g, 2.12 mmol) were combined. The reaction mixture was stirred under N_2 and heated to 150 °C for 24 hours. The resulting mixture was cooled to room temperature, ice cold water was added to precipitate the reaction, and the slurry was separated via vacuum filtration. The resulting dark red precipitate was washed with ethanol, methanol, and water to remove any residual DMF and aniline material. The dark red precipitate was collected as the desired product.

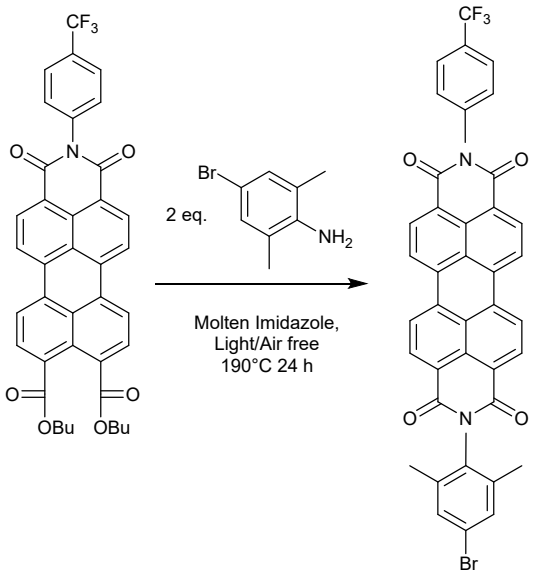
(Known method for novel product) Average yield: 0.486 g (76%). ^{1}H NMR (400 MHz, DMSO-D_6) δ 8.76 (d, J = 8.1 Hz, 4H), 8.49 (d, J = 7.9 Hz, 4H), 8.05 (d, J = 7.9 Hz, 4H), 7.72 (d, J = 8.6 Hz, 2H), 7.37 (d, J = 8.6 Hz, 2H. ^{19}F NMR (376 MHz, CDCl3, 25 °C): δ -62.67 (s 3F). Exact MS (-CI): *m/z* calculated for $C_{37}H_{16}BrF_3N_2O_4$, 688.02 *m/z*; observed 688.02 *m/z*. IR solid state (ν, cm^{-1}): 1713 (s), 1705 (s), 1636 (s), 1591 (m), 1246 (s), 1243 (m), 1240 (s), 1128 (m), 1122 (m), 1115(m), 1003 (m), 836 (s), 754 (s), 595 (m).



Scheme 2.12 Reaction scheme for converting the 4-trifluoromethyl aniline PMA derivative to non-symmetric the 4-bromophenylethylamine-imide derivative.

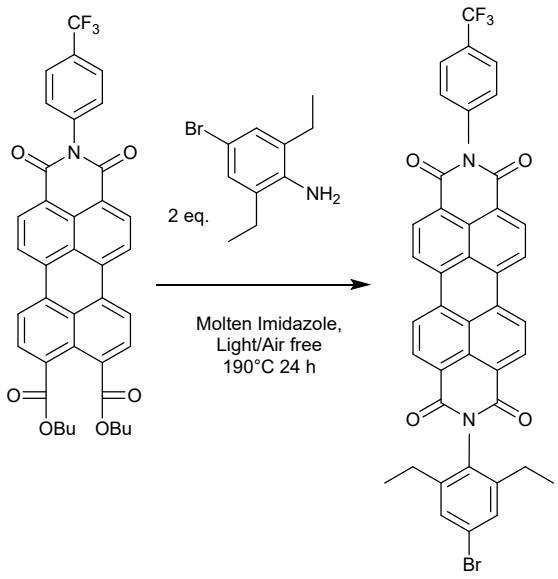
An amount of 4-Trifluoromethyl aniline monoanhydride perylene 3,4,9,10-tetracarboxylic acid (0.500 g, 0.91 mmol), 60 mL of *N*-methyl-2-pyrrolidone (NMP), glacial acetic acid (0.8 mL, 10.3 mmol), and 4-bromophenylethylamine (0.32 mL, 2.06 mmol) were combined. The reaction mixture was stirred under N_2 and heated 120 °C for 24 hours. The resulting mixture was cooled to room temperature, poured into water, and the resulting precipitate was isolated via Büchner funnel vacuum filtration. The maroon precipitate was washed with several aliquots of water to remove any residual NMP. The maroon reaction precipitate was collected as the desired product. (Known method for novel product) Average yield: 0.626 g (94%). ^{1}H NMR (399 MHz, DMSO-D_6) δ 8.19 (s, 4H), 7.91 (s, 3H), 7.68 (s, 2H), 7.46 (s, 3H), 7.19 (s, 2H), 4.10 (d, J = 7.3 Hz, 1H), 2.83 (s, 2H) ^{19}F NMR (376 MHz, CDCl3, 25 °C): δ -62.67 (s 3F). Exact MS (-CI): *m/z* calculated for $C_{39}H_{20}BrF_3N_2O_4$, 716.07 *m/z*; observed 716.06 *m/z*. IR solid state (ν, cm^{-1}): 2973 (m), 2767 (m),

1713 (s), 1705 (s), 1604 (s), 1642 (m), 1258 (s), 1253 (m), 1120 (m), 1121 (w), 1111 (w), 1007 (m), 815 (s), 766(s), 548 (m).



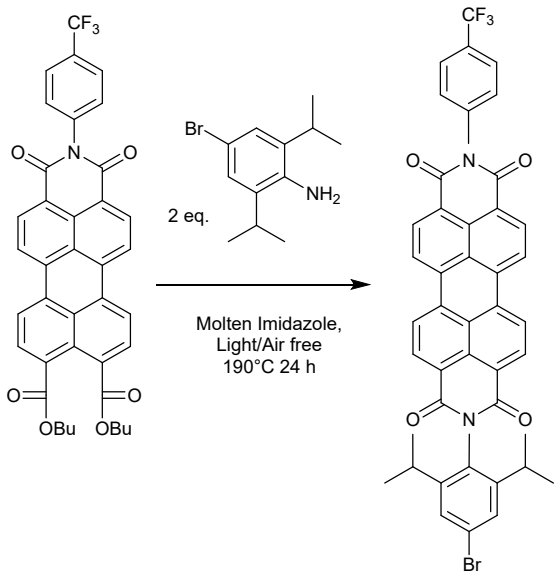
Scheme 2.13 Reaction scheme for converting non-symmetric the 4-trifluoromethyl aniline-imide dibutylester derivative to non-symmetric the 4-bromo-2,6-dimethylaniline- imidederivative.

An amount of 4-Trifluoromethyl aniline-imide dibutylester perylene 3,4,9,10-tetracarboxylic acid 0.256 g, 0.385 mmol), 4-bromo-2,6-dimethylaniline (0.281 g 1.43 mol), and imidazole (2.5 g) were added to a 50 mL Schlenk flask. The reaction mixture was stirred under N_2 in the dark, heated to 190 °C, and reacted for 20 hours. The imidazole melted once the reaction reached 140 °C and the solution color changed from dark red to black. After 20 hours the reaction was cooled to room temperature, 25 mL of ethanol and 30 mL of 2 M HCl were added to the flask and the solution was stirred for 4 hours. The resulting precipitate was isolated via Büchner funnel vacuum filtration and rinsed with ethanol then water. (Known method for novel product) Average yield: 0.276 g (95%). ^{1}H NMR (400 MHz, CDCl3, 25 °C): δ 8.83 – 8.73 (m, 8H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.50 (d, 2H), 7.05 (d, 2H), 2.95 (d, *J* = 3.5 Hz, 3H), 2.88 (d, *J* = 3.3 Hz, 3H), 2.14 (d, *J* = 3.3 Hz, 2H), 1.54 (d, *J* = 3.1 Hz, 6H). ^{19}F NMR (376 MHz, CDCl3, 25 °C): *δ* -62.67 (s 3F). Exact MS (-CI): *m/z* calculated for $C_{39}H_{20}BrF_3N_2O_4$, 716.06 *m/z*; observed 716.06 *m/z*. IR solid state (ν, cm^{-1}): 2983 (m), 2882 (m), 1754 (s), 1735 (m), 1631 (m), 1629 (m), 1585 (m), 1516 (s), 1355 (m), 1171 (m), 1120 (m), 1007 (m), 810 (s), 751 (s), 749 (w), 538 (m).



Scheme 2.14 Reaction scheme for converting the non-symmetric 4-trifluoromethyl aniline-imide dibutylester derivative to the non-symmetric 4-bromo-2,6-diethylaniline- imide derivative.

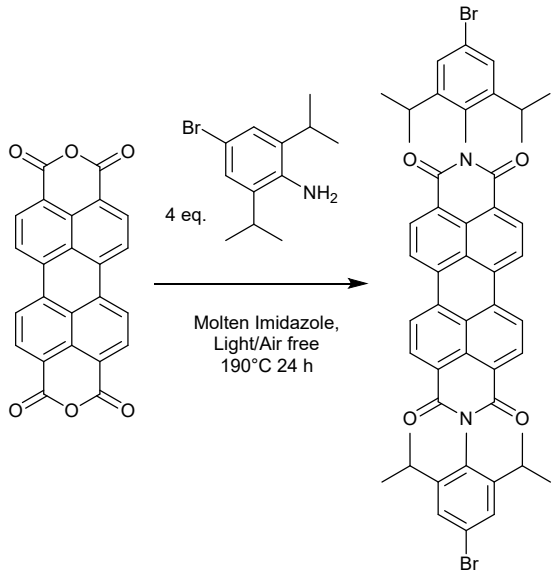
An amount of 4-trifluoromethyl aniline-imide dibutylester perylene 3,4,9,10-tetracarboxylic acid 0.259 g, 0.389 mmol), 4-bromo-2,6-diethylaniline (0.3 mL, 1.50 mmol), and imidazole (2.5 g) were added to a 50 mL Schlenk flask. The reaction mixture was stirred under N_2 in the dark, heated to 190 °C, and reacted for 20 hours. The imidazole melted once the reaction reached 140 °C and the solution color changed from dark red to black. After 20 hours the reaction was cooled to room temperature, 25 mL of ethanol and 30 mL of 2 M HCl were added to the flask, and the solution was stirred for 4 hours. The resulting precipitate was isolated via Büchner funnel vacuum filtration and rinsed with ethanol followed by water. (Known method for novel product) Average yield: 0.282 g (97%). ^{1}H NMR (400 MHz, CDCl3, 25 °C): δ 8.67 (m, 6H), 8.50 (m, 2H), 7.92 (t, 1H) 7.84 (d, 1H), 7.62 (s 2H), 7.48 (d, 2H), 2.21 (m, 4H), 0.5 (m, 6H). ^{19}F NMR (376 MHz, CDCl3, 25 °C): δ -62.67 (s 3F). Exact MS (-CI): *m/z* calculated for $C_{41}H_{24}BrF_3N_2O_4$, 744.09 *m/z*; observed 744.09 *m/z.* IR solid state (ν, cm^{-1}): 2983 (m), 2878 (m), 1755 (s), 1736 (s), 1632 (m), 1630 (m), 1584 (m), 1518 (s), 1335 (m), 1176 (m), 1122 (m), 1001 (m), 815(s), 753 (s), 756 (w), 535 (m).



Scheme 2.15. Reaction scheme for converting the non-symmetric 4-trifluoromethyl aniline-imide dibutylester derivative to the non-symmetric 4-bromo-2,6-diisobutylaniline – imide derivative.

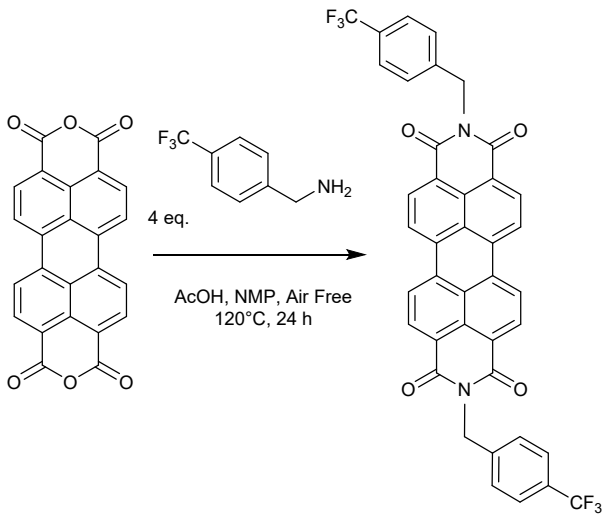
An amount of 4-Trifluoromethyl aniline-imide dibutylester perylene 3,4,9,10-tetracarboxylic acid (0.259 g, 0.389 mmol), 4-bromo-2,6-diisobutylaniline (0.3 mL, 1.127 mmol), imidazole (2.5 g) were added to a 50 mL Schlenk flask. The reaction mixture was stirred under N_2 in the dark, heated to 190 °C, and reacted for 20 hours. The imidazole melted once the reaction reached 140 °C and the solution color changed from dark red to black. After 20 hours the reaction was cooled to room temperature, and 25 mL of ethanol and 30 mL of 2 M HCl was added to the flask and stirred for 4 hours. The precipitate was isolated via Büchner funnel vacuum filtration and rinsed with ethanol followed by water. (Known method for novel product) Average yield: 0.257 g (86%). ^{1}H NMR (399 MHz, BENZENE-D_6) δ 7.29 (s, 2H), 6.99 (d, J = 7.2 Hz, 2H), 6.95 (d, J = 7.6 Hz, 8H), 6.90 (s, 2H), 3.51 (s, 2), 2.05 (s, 12H), ^{19}F NMR (376 MHz, CDCl3, 25 °C): δ -62.67 (s 3F). Exact MS (-CI): *m/z* calculated for $C_{31}H_{28}BrF_3N_2O_4$, 772.12 *m/z*; observed 772.12 *m/z*. IR solid state (ν, cm^{-1}): 2985 (m), 2874 (m), 1756 (s), 1732 (s), 1637 (m), 1631 (m), 1587 (m), 1518 (s), 1337 (m), 1177 (m), 1124 (m), 1003 (m), 818 (s), 757 (s), 756 (w), 533 (m).

3. Symmetric Procedures



Scheme 3.1. Reaction scheme for the conversion of dianhydride derivative to the symmetric 4-bromo-2,6-diisobutylaniline imide derivative.

An amount of dianhydride perylene 3,4,9,10-tetracarboxylic acid (0.259 g, 0.64 mmol), 4-bromo-2,6-diisobutylaniline (0.5 mL, 2.56 mmol), and imidazole (2.5 g) were added to a 50 mL Schlenk flask. The reaction mixture was stirred under N_2 in the dark, heated to 190 °C, and reacted for 20 hours. The imidazole melted once the reaction reached 140 °C and the solution changed color from dark red to black. After 20 hours, the reaction was cooled to room temperature, and 25 mL of ethanol and 30 mL of 2 M HCl were added to the flask and stirred for 4 hours. The precipitate was isolated via Büchner funnel vacuum filtration and rinsed with ethanol followed by water.(Known method and known product) Average yield: 0.448 g (80%). ^{1}H NMR (399 MHz, ACETONE-D_6) δ 9.04 (d, J = 8.1 Hz, 2H), 8.70 (dd, J = 8.3, 1.9 Hz, 3H), 7.51 (dd, J = 4.7, 2.1 Hz, 3H), 7.36 (dd, J = 7.8, 2.0 Hz, 1H), 7.23 (s, 1H), 2.93 – 2.83 (m, 4H), 1.13 (td, J = 14.7, 8.5, 3.6 Hz, 24H) Exact MS (-CI): *m/z* calculated for $C_{48}H_{40}Br_2N_2O_4$, 866.14 *m/z*; observed 866.14 *m/z*. IR solid state (ν, cm^{-1}): 2984 (m), 2874(m), 1756 (s), 1733 (s), 1638 (m), 1633 (m), 1586(m), 1519 (s), 1335 (m), 1178 (m), 1129 (m), 1001 (m), 819 (s), 753 (s), 752 (w), 536 (m).



Scheme 3.2 Reaction scheme for the converting the dianhydride derivative to the symmetric 4-bromo-2,6-diisobutylaniline-imide derivative.

An amount of 4-(Trifluoromethyl)benzyl-imide monoanhydride perylene 3,4,9,10-tetracarboxylic acid (0.5 g, 0.91 mmol), 60 mL of *N*-methyl-2-pyrrolidone (NMP), glacial acetic acid (0.8 mL, 10.3 mmol), and 4-bromophenylethylamine (0.3 mL, 0.00199 mol) were combined. The reaction mixture was stirred under N_2 and heated 120 °C for 24 hours. The resulting mixture was cooled to room temperature, and poured into water, yielding a precipitate that was isolated via Büchner funnel vacuum filtration. The brown precipitate was washed with several aliquots of water to remove any residual NMP. The red precipitate was collected as the desired product. (Known method for known product) Average yield: 2.47 g (92%). ^{1}H NMR (400 MHz, CDCl3, 25 °C): δ 8.21 (d, 4H), 7.85 (d, 4H), 7.54 (d, 4H), 7.17 (d, 4H), 4.34 (t, 4H). ^{19}F NMR (376 MHz, CDCl3, 25 °C): δ -62.67 (s 6F). Exact MS (-CI): *m/z* calculated for $C_{40}H_{20}F_6N_2O_4$, 706.13 *m/z*; observed 706.13 *m/z*. IR solid state (ν, cm^{-1}): 2954 (m), 2763 (m), 1712 (s), 1705 (s), 1603 (s), 1641 (m), 1258 (s), 1245 (s), 1120 (m), 1107 (w), 1123 (w), 1005 (m), 815 (s), 757(s)., 598 (m), 376 (m).

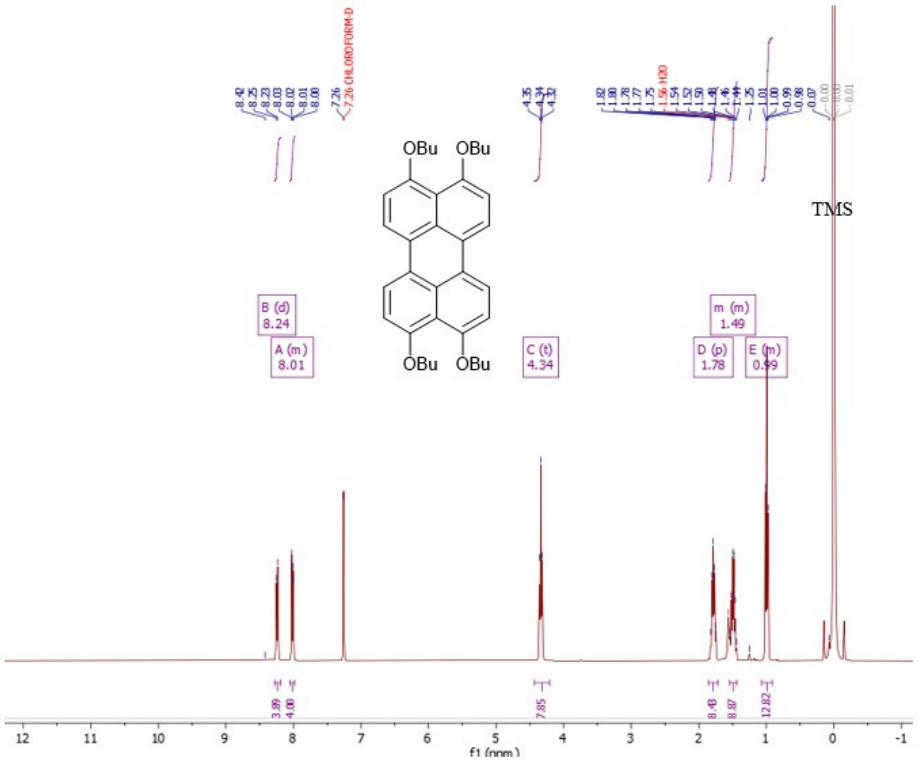


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of anhydride opening as performed in **Scheme 2.1**

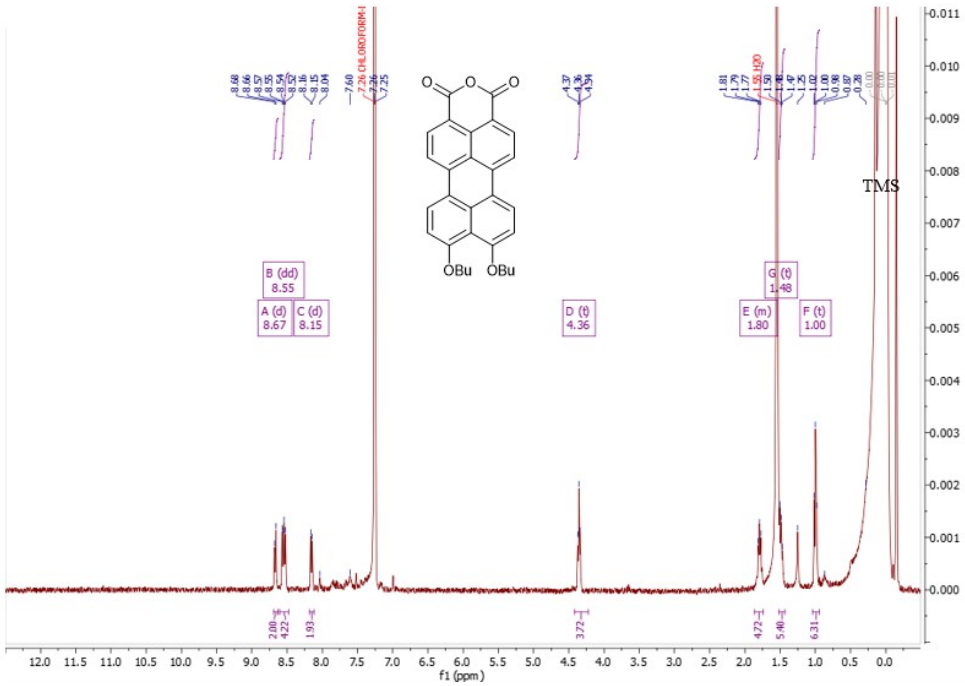


Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of single anhydride closure as performed in **Scheme 2.2**

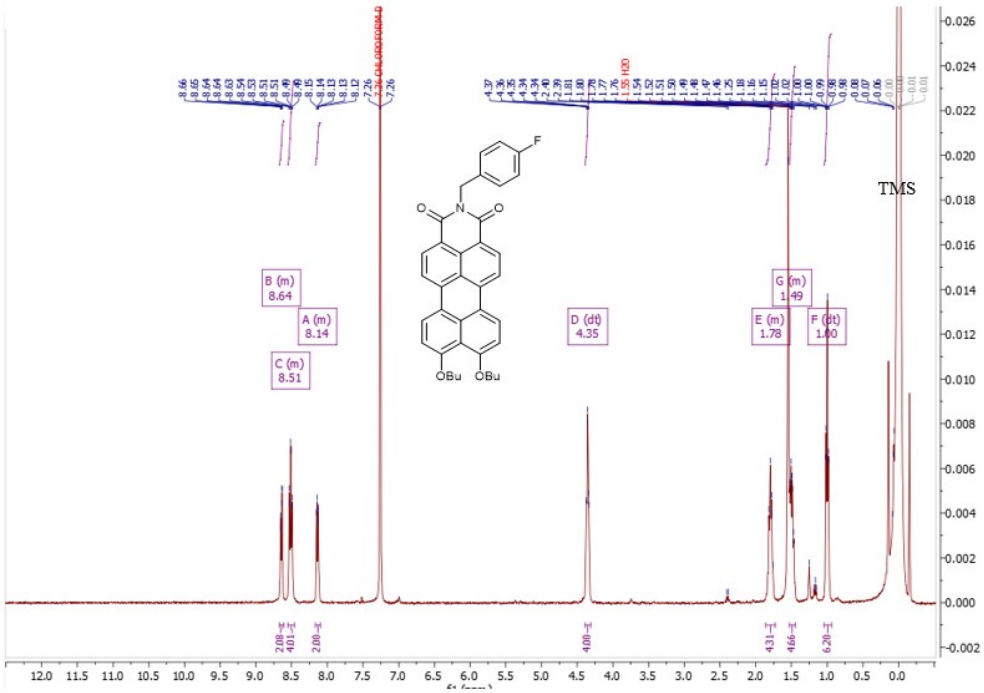


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of imidization as performed in **Scheme 2.3**

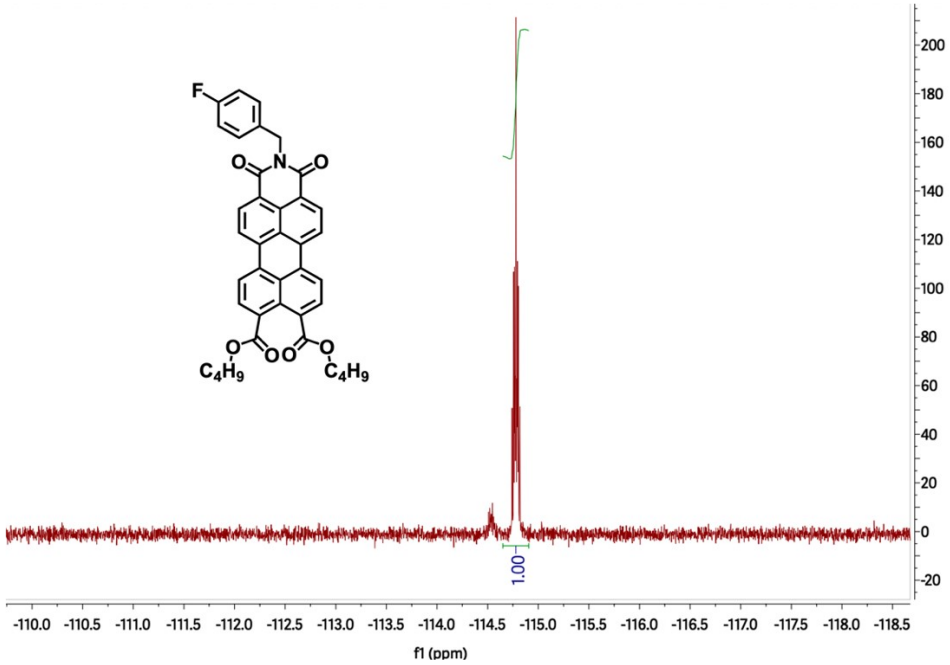


Figure S4. ^{19}F NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of imidization as performed in **Scheme 2.3**

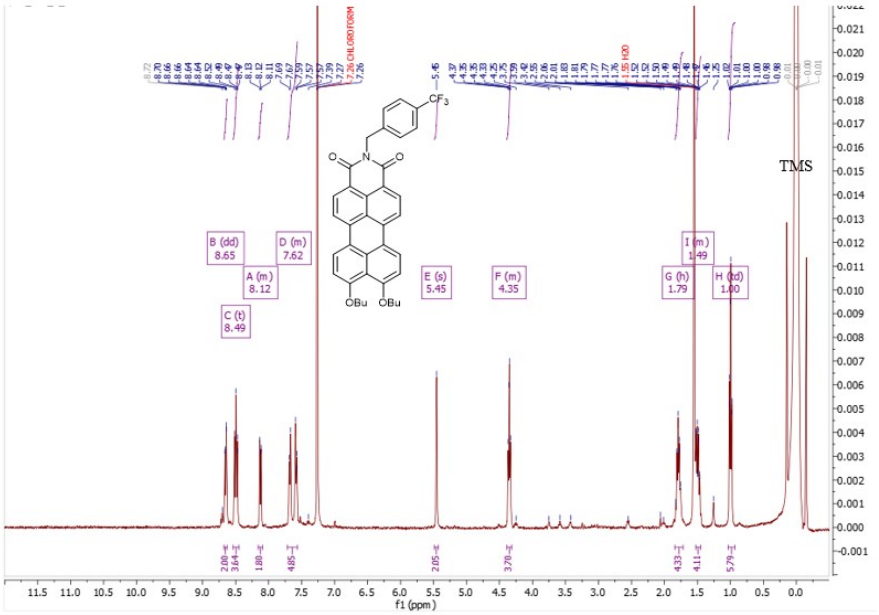


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of imidization as performed in **Scheme 2.5**.

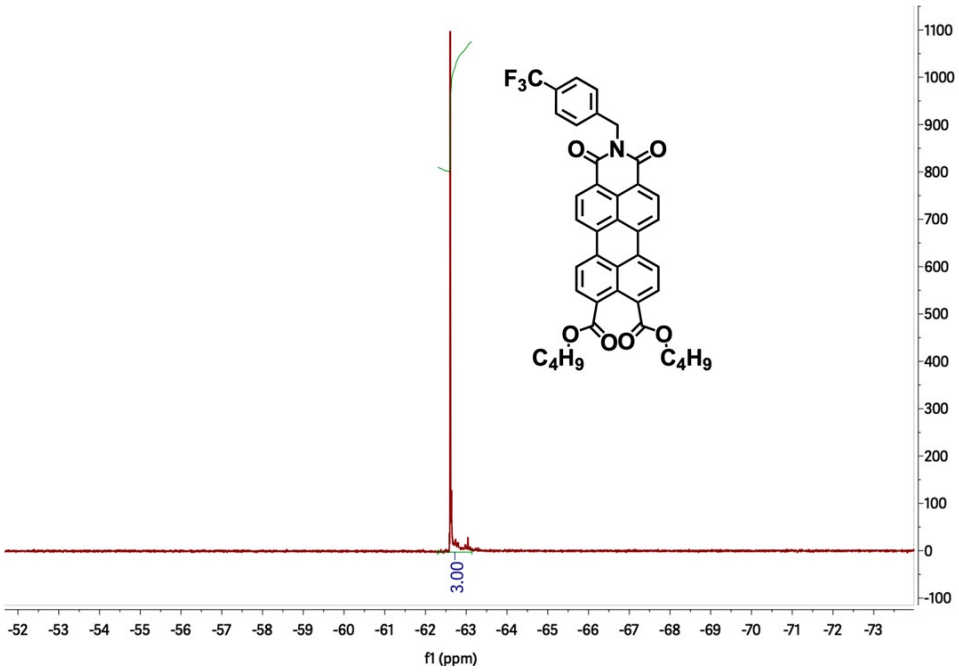


Figure S6. ^{19}F NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of imidization as performed in **Scheme 2.5**

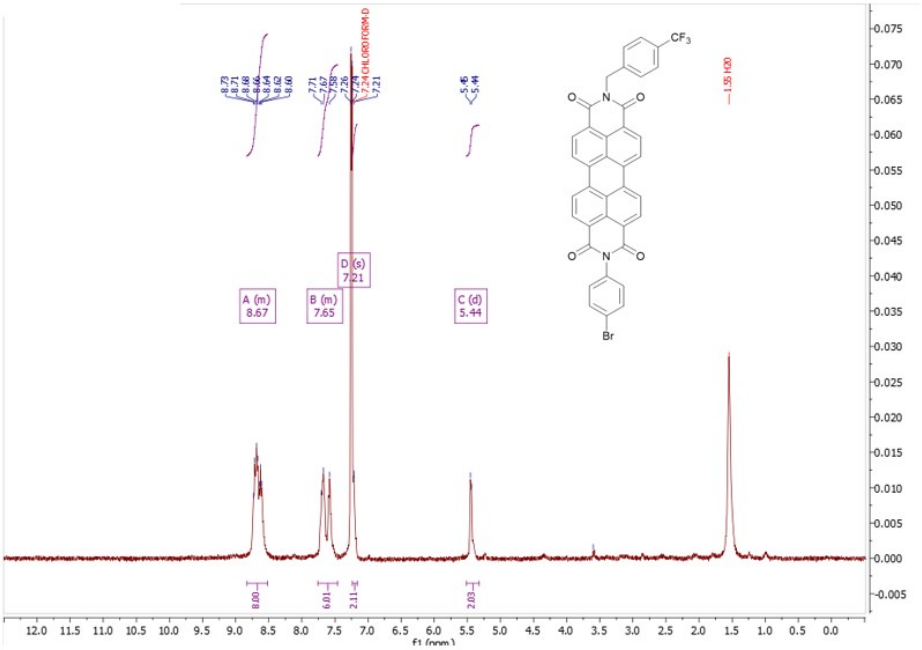


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of imidization as performed in **Scheme 2.7**

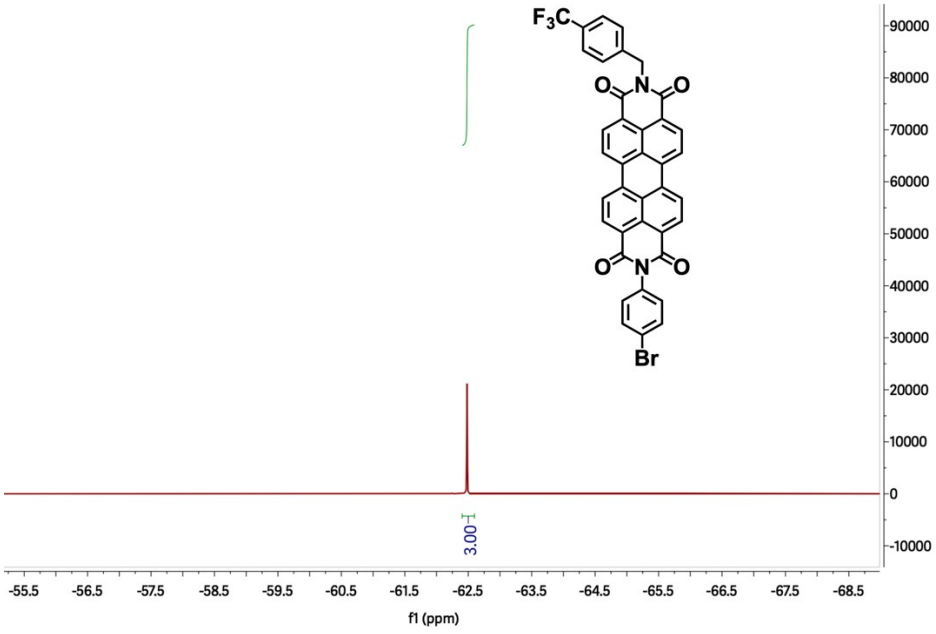


Figure S8. ^{19}F NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of imidization as performed in **Scheme2.7**

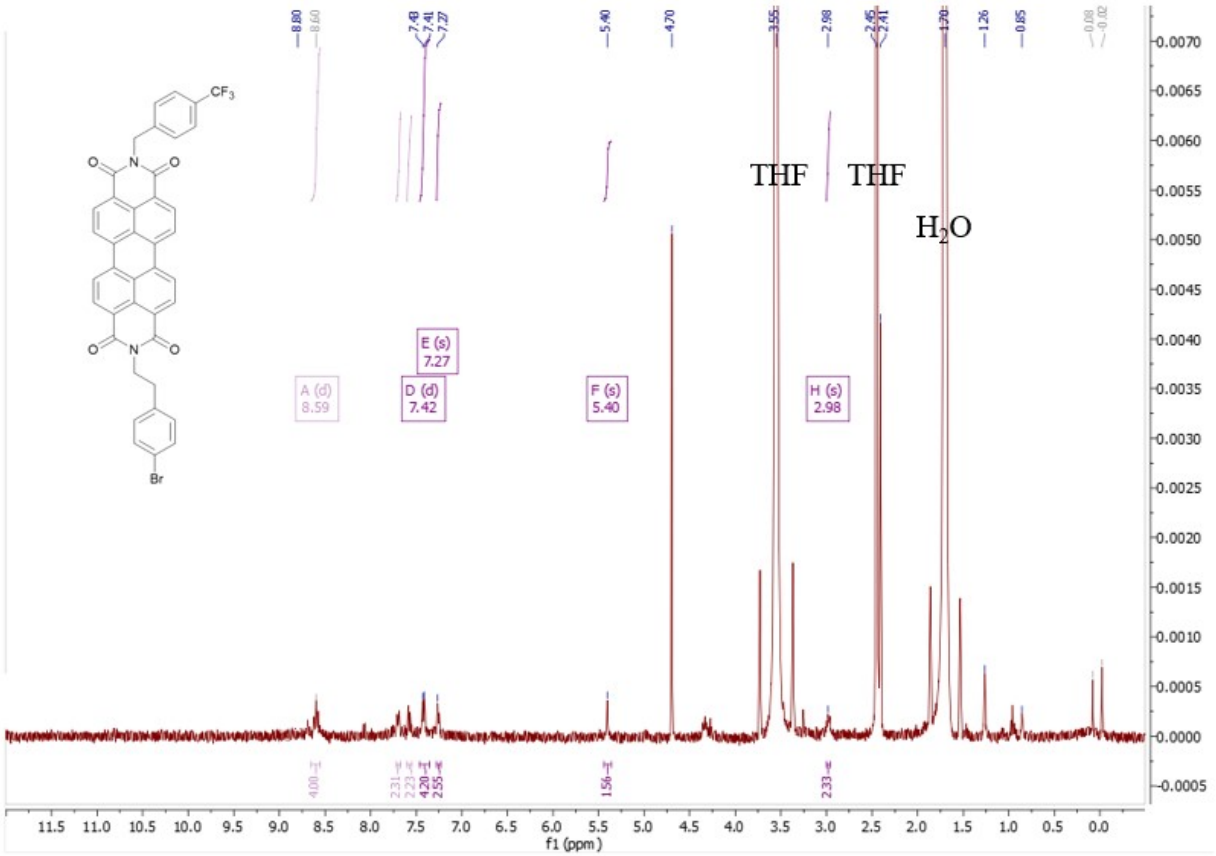


Figure S9. ^{1}H NMR spectrum (400 MHz, THF-$d_{8,}$ 25 °C) of imidization as performed in **Scheme 2.8**

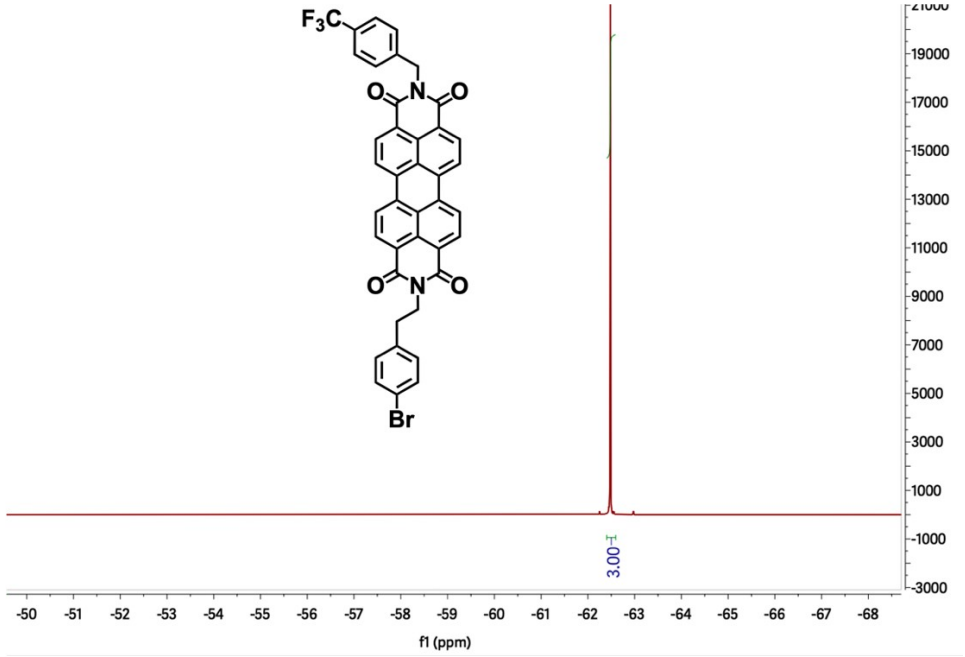


Figure S10. ^{19}F NMR spectrum (376 MHz, $CDCl_{3,}$ 25 °C) of imidization as performed in **Scheme 2.8**.

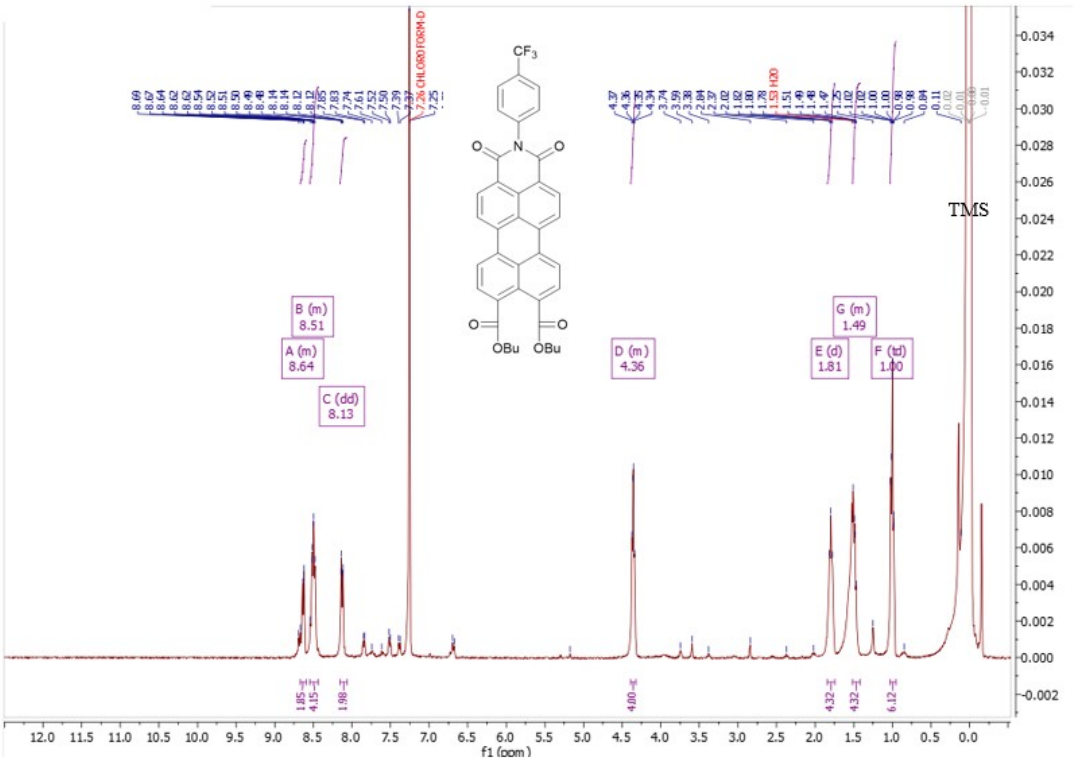


Figure S11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of imidization as performed in **Scheme 2.9**

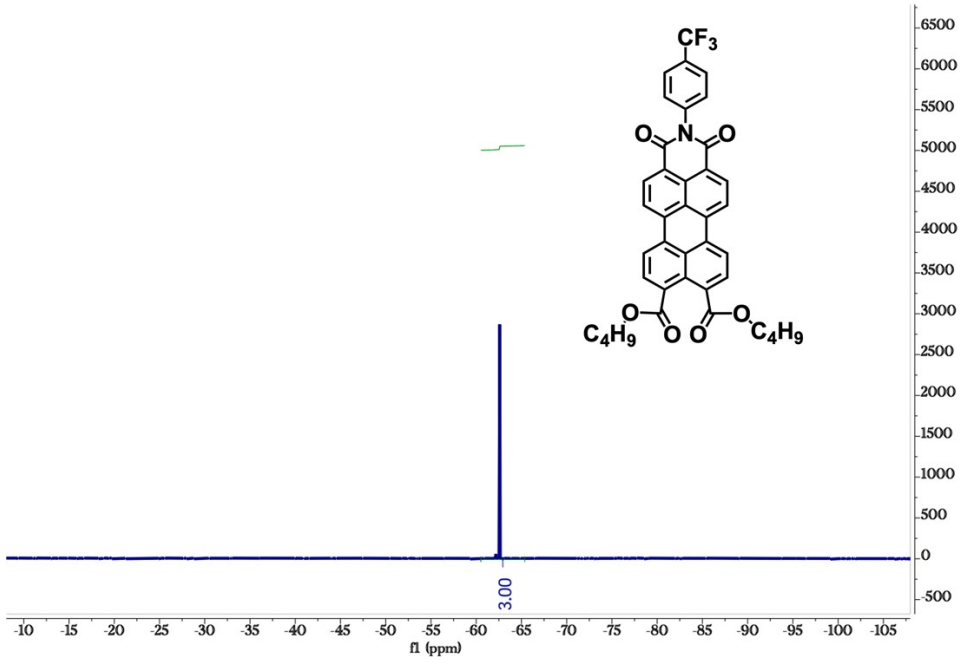


Figure S12. ^{19}F NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of imidization as performed in **Scheme 2.9**

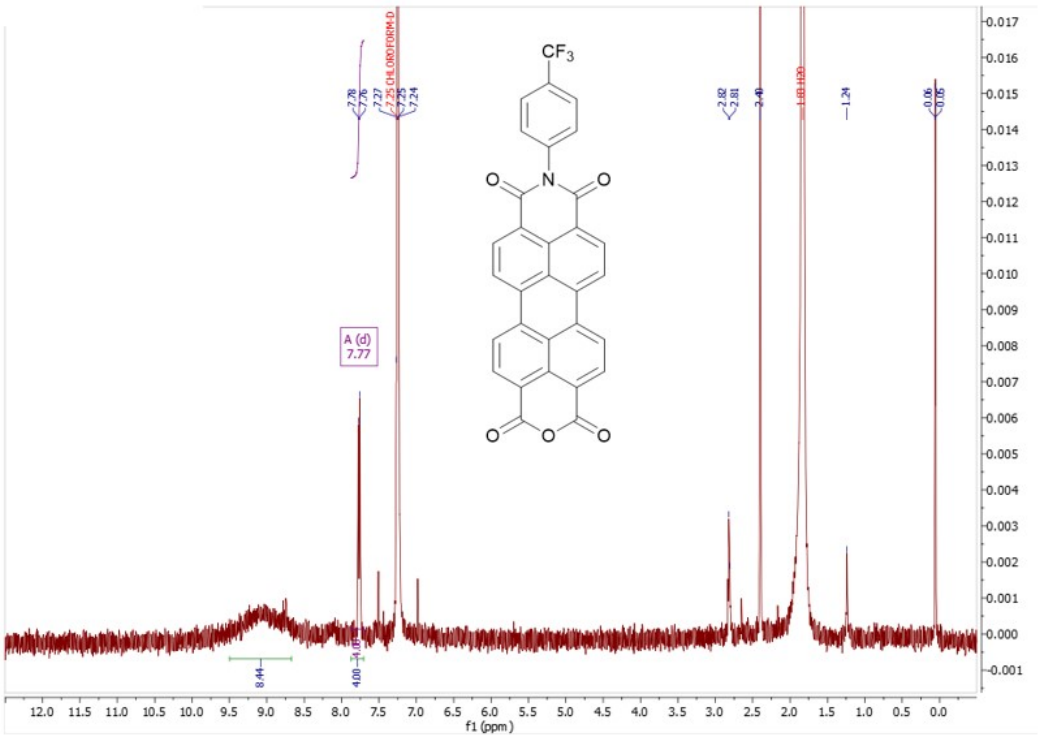


Figure S13. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of anhydride closing as shown in **Scheme 2.10**

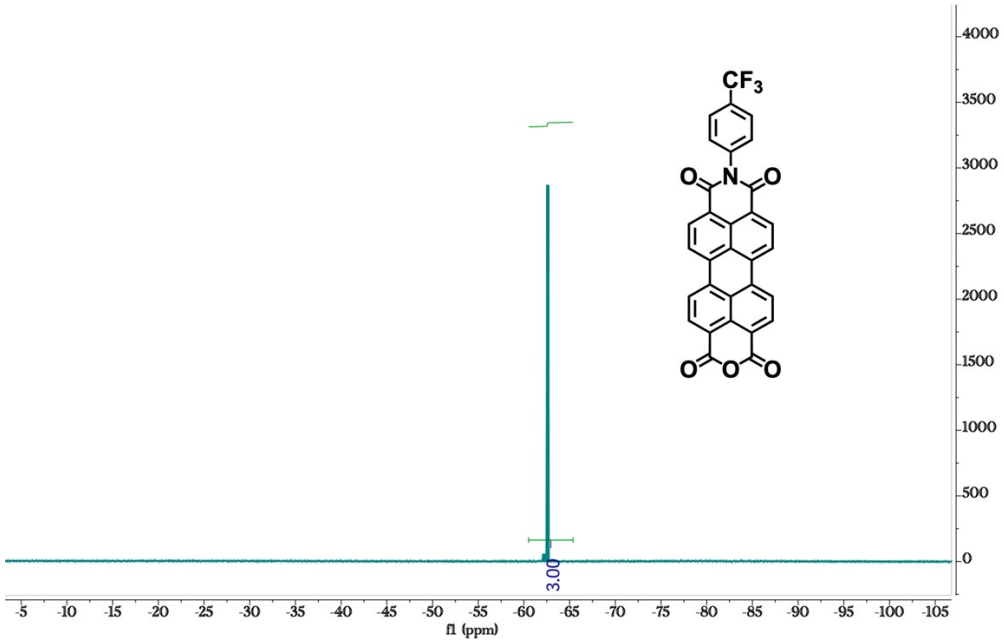


Figure S14. ^{19}F NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of anhydride closing as shown in **Scheme 2.10**

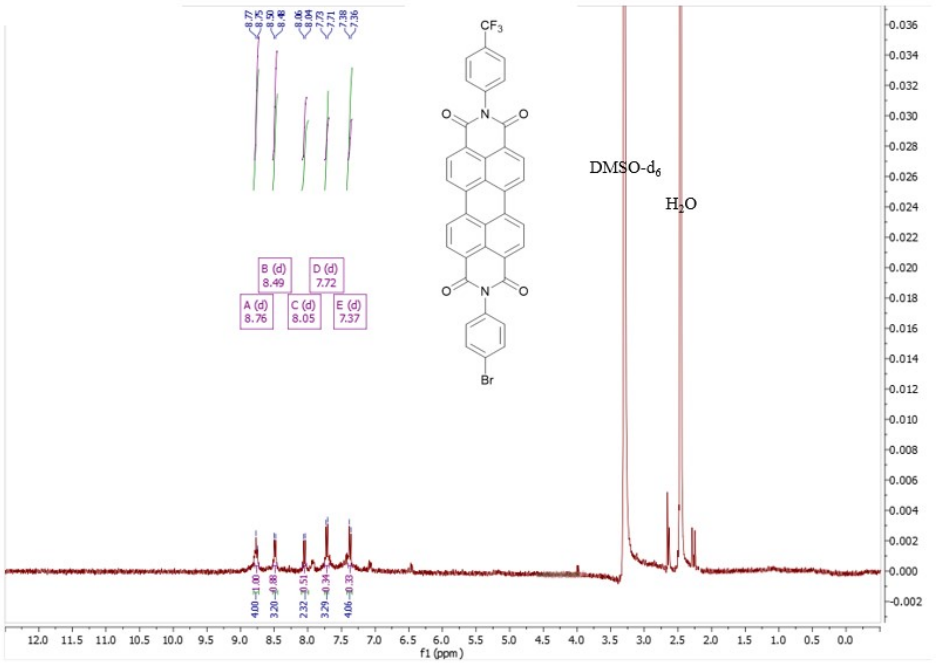


Figure S15. ^{1}H NMR spectrum (400 MHz, DMSO-d_6, 25 °C) of imidization as shown in **Scheme 2.11**

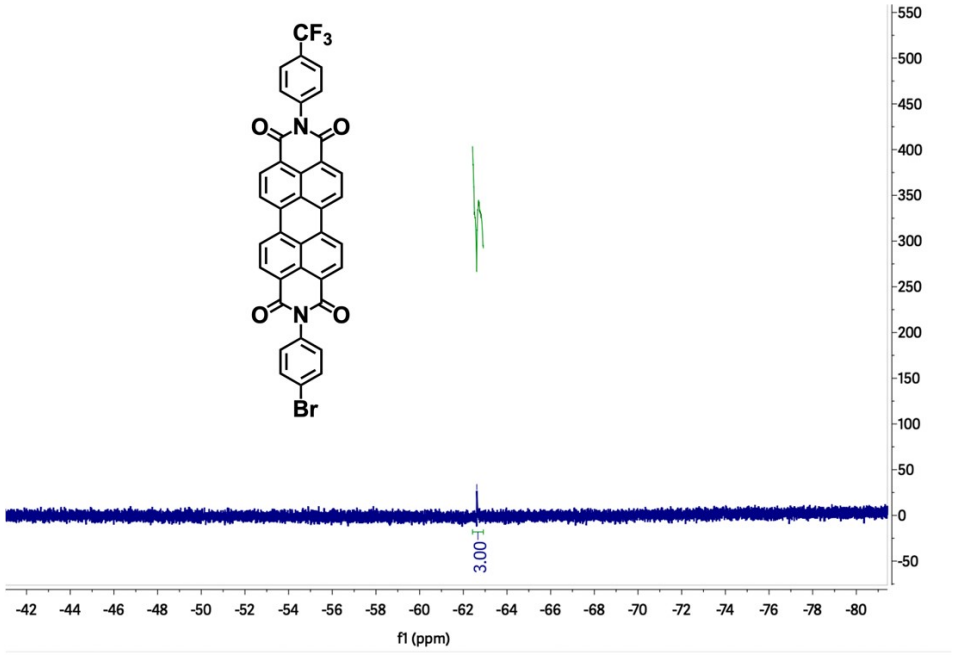


Figure S16. ^{19}F NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of imidization as shown in **Scheme 2.11**

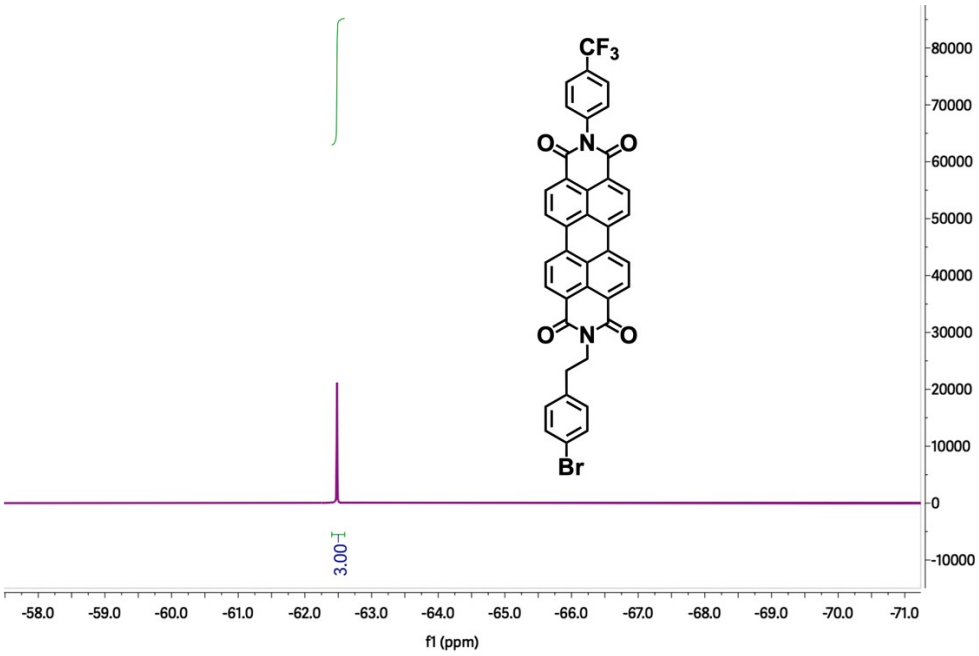


Figure S17. ^{19}F NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of imidization as shown in **Scheme 2.12**

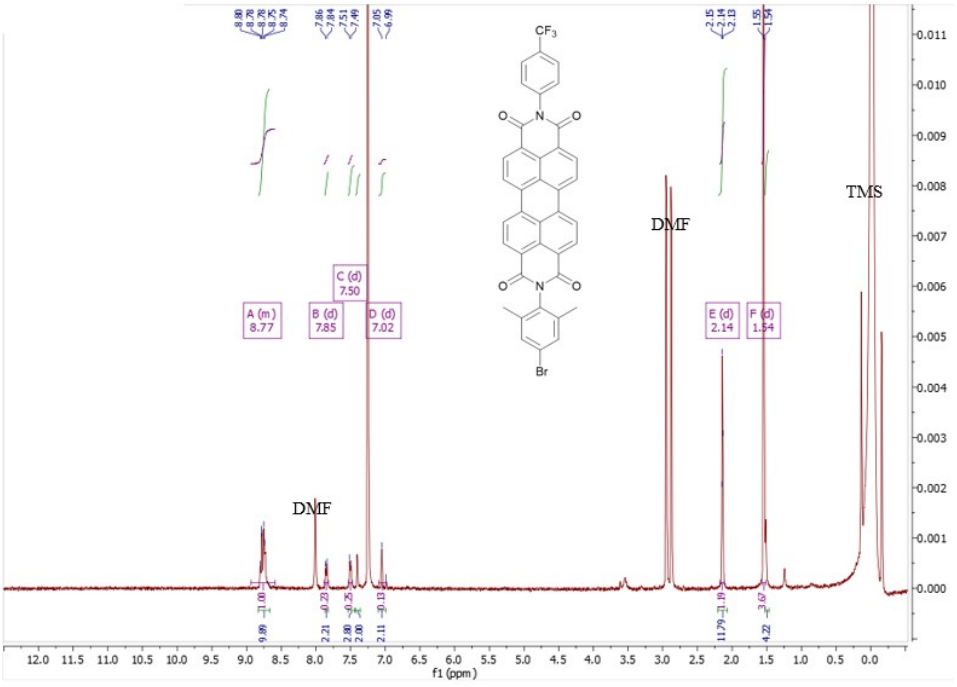


Figure S18. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 25 °C) of imidization as shown in **Scheme 2.13**

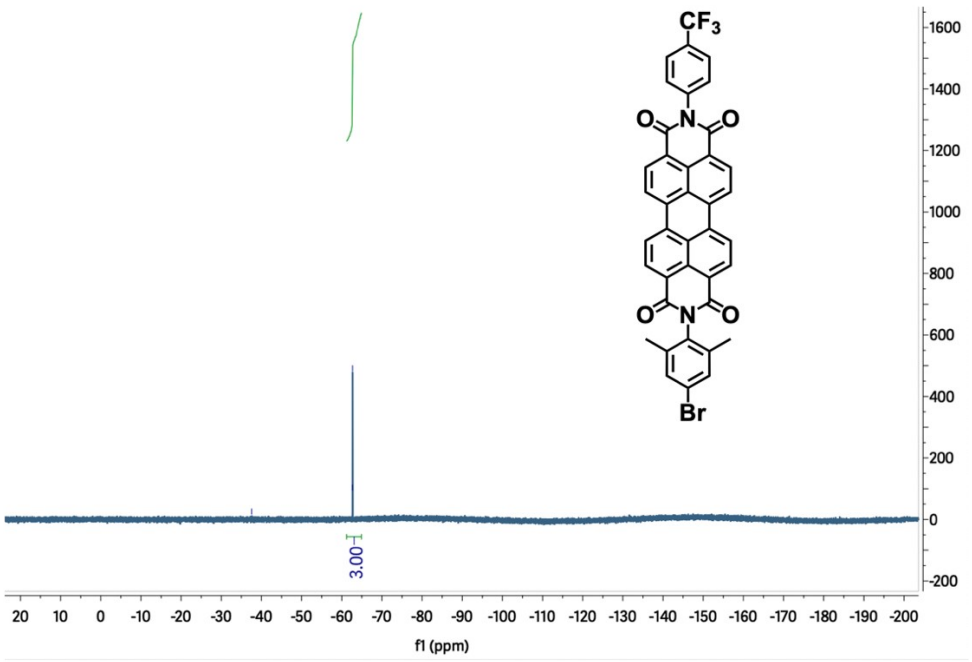


Figure S19. ^{19}F NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of imidazole method as shown in **Scheme 2.13**

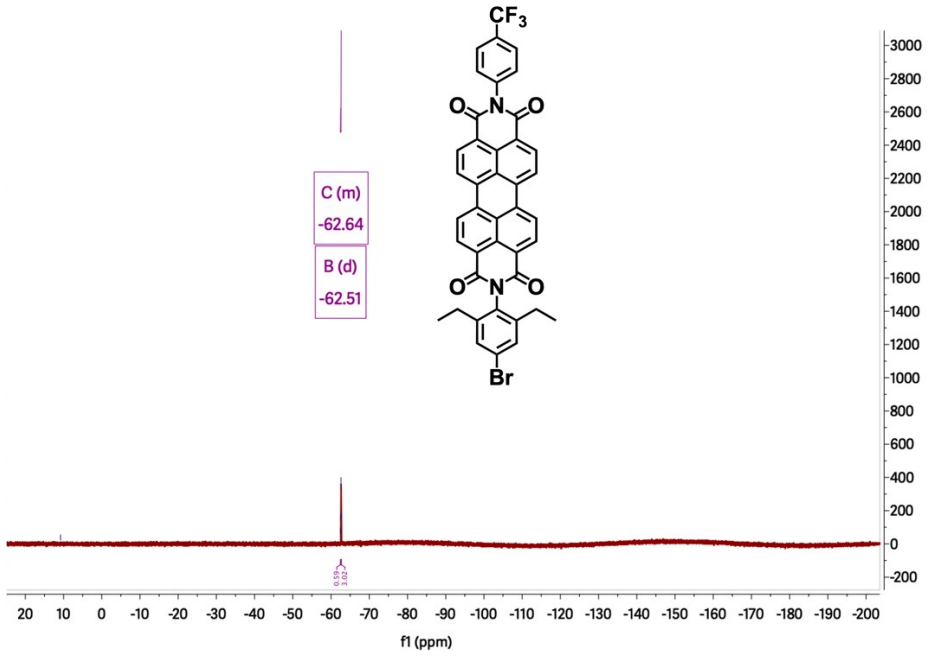


Figure S20. ^{19}F NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of imidazole method as shown in **Scheme 2.14**

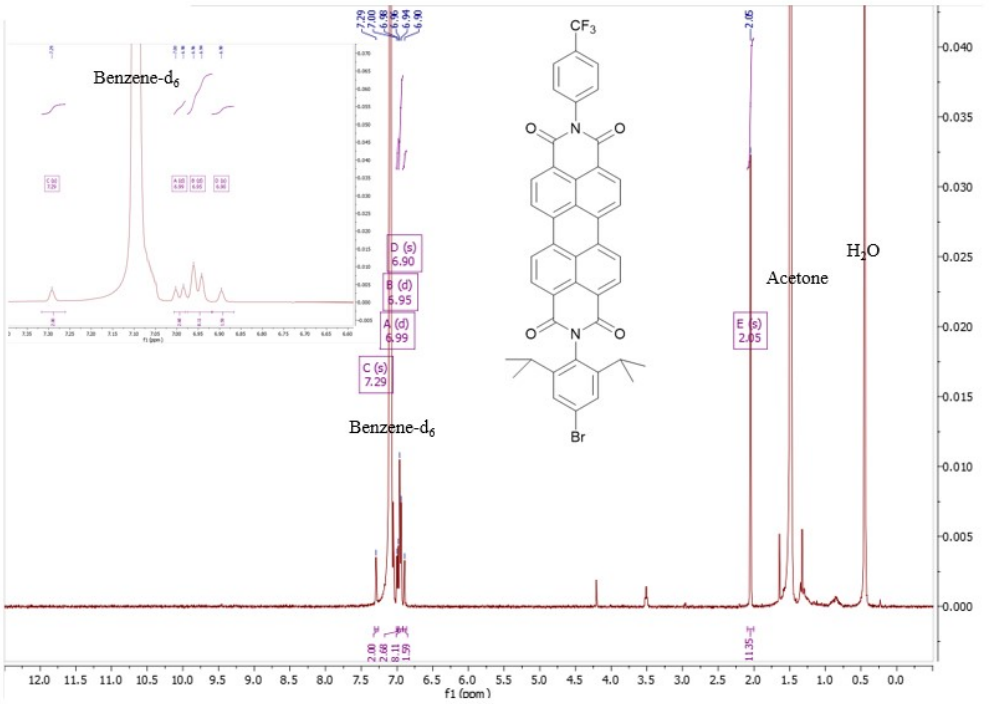


Figure S21. ^{1}H NMR spectrum (400 MHz, benzene-d_6, 25 °C) of imidazole method as shown in **Scheme 2.15**

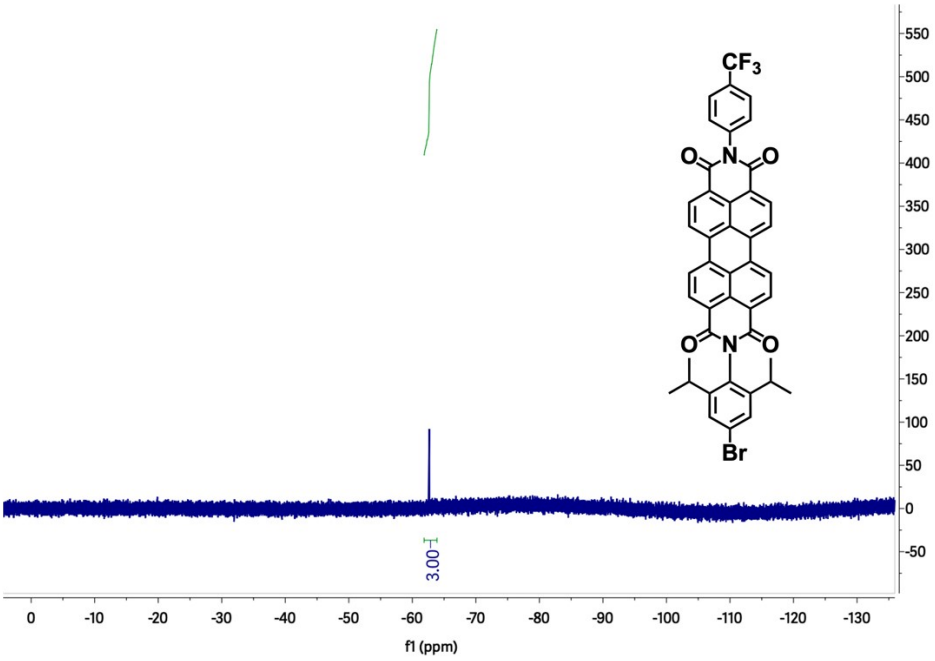


Figure S22. ^{19}F NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of imidazole method as shown in **Scheme 2.15**

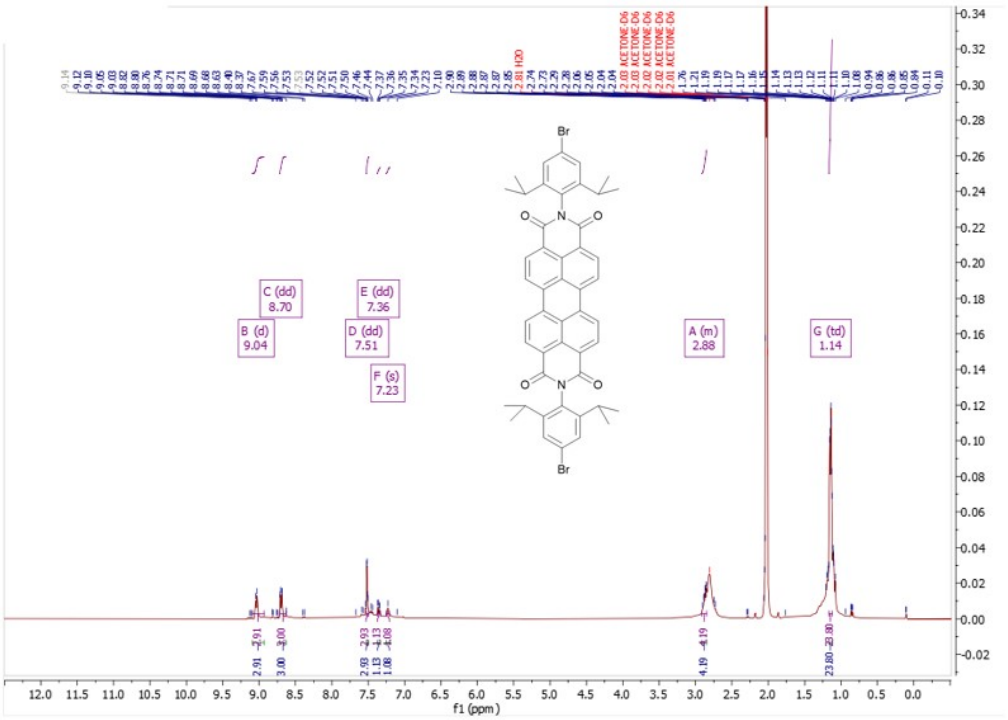


Figure S23. ^{1}H NMR spectrum (400 MHz, Acetone-d_6, 25 °C) of imidization as show in **Scheme 3.1**

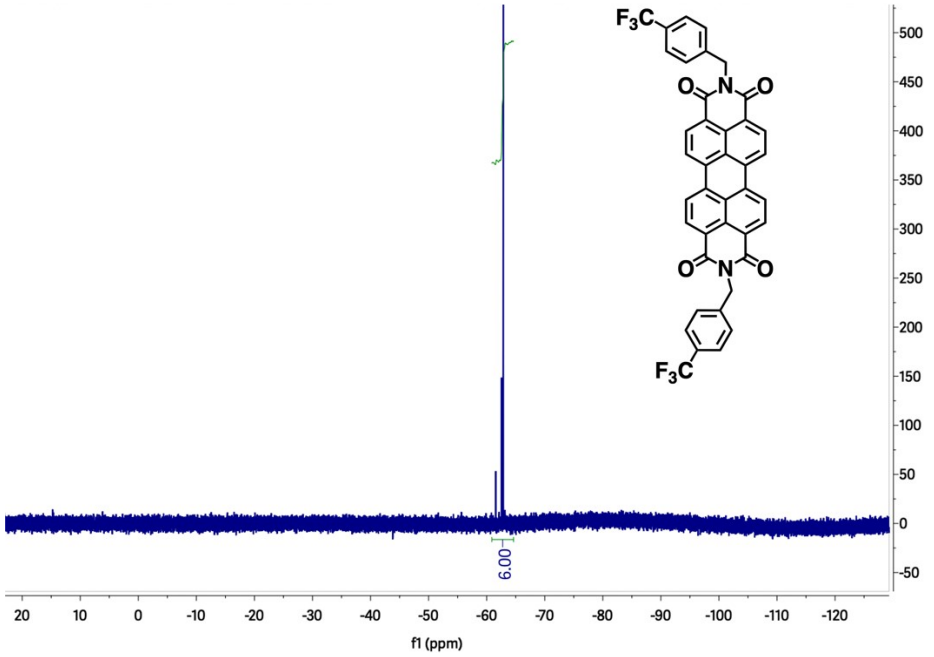


Figure S24. ^{19}F NMR spectrum (376 MHz, $CDCl_3$, 25 °C) of imidization as show in **Scheme 3.2**