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ORIGINAL ARTICLE

The efficient synthesis of N-fused coronene analogs and a related polyimide with near-infrared absorption

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A novel technique to synthesize N-fused coronene analogs was developed using the conventional thermal cycloaddition of perylene diimide with several 1,2,4-triazoline-3,5-diones. The cycloaddition occurred twice, primarily yielding a bis-adduct under optimized reaction conditions. ^{1}H-nuclear magnetic resonance spectroscopy confirmed the transformation of the perylene unit with a polyimide backbone to a N-fused coronene unit. The N-fused coronene derivatives exhibited a wide absorption range from 600 to 850 nm and a low band gap of 1.3 eV.
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INTRODUCTION

Coronene is a polycyclic aromatic hydrocarbon with electrons that are perfectly delocalized among the six peri-fused benzene rings. Coronene molecules are stacked closely in parallel with one another because of their unique flat electronic structure, which allows for excellent self-assembly and increasing electron mobility.[1–3] Graphene and carbon nanotubes with excellent electron conductivity are considered to be expansions of the coronene structure. Many attempts have been made to synthesize coronene derivatives with different electrical and electronic characteristics.[3–6] The addition of electron-withdrawing imide groups to coronene produced an n-type semiconductor material with liquid crystalline self-assembly characteristics.[7] To produce carbon derivatives of coronene, the transition metal-catalyzed coupling of bromo-substituted perylene and other aromatic moieties is popular.[8–11] The fused cyclic structure of coronene is prepared through a pericyclic reaction, and the thermal coupling reaction between the perylene imides and dienophiles followed by the *in situ* aromatization produces the coronene structure.[12,13] Electron-deficient coronene octacarboxylic tetraimides have been developed for columnar liquid crystals.[4,5]

Producing coronene derivatives via thermal synthesis is limited because of the low reactivity of electron-deficient mono-adducts. H Bock and colleagues isolated a bis-adduct using maleimide as a dienophile instead of maleic anhydride.[4,5] Many studies of coronene analogs have focused on their applications in photovoltaic devices, organic field effect transistors and liquid crystals.[8–11] These applications take advantage of the electronic properties of flat molecules that allow for pi-overlap. Z Wang and K Müllen examined the extension of the aromatic core on a perylene bay.[8–11] Significant optical changes were achieved by extending the length. Heterocyclic extensions, such as the N- and S-cycle, were used for

their molecular recognition or optical absorption properties.[8–14] H Langhals *et al.*[12,13] reported a triazolinedione adduct of perylene imides, which absorbs near-infrared light. The introduction of electron-donating nitrogen to a perylene imide often involves a strong bathochromic shift.[15] Despite the interest in this triazolinedione adduct, the product was formed in low yield.[12,13] This research presents a practical synthesis of the triazoline adducts of perylene imides using various reaction conditions, which is then applied for the preparation of a polyimide with near-infrared absorption.

EXPERIMENTAL PROCEDURE

Materials

All reagents were purchased from Sigma-Aldrich Chemical (Yongin, Korea), and the reagent-grade solvents were dried when necessary and purified by vacuum distillation. Perylene-3,4,9,10-tetracarboxylic dianhydride and 4,4'-oxydiphthalic anhydride were purified using a conventional sublimation process. The products were purified using silica gel column chromatography (Merck, Seoul, Korea, 250–430 mesh).

Characterizations

For internal reference, the ^{1}H-nuclear magnetic resonance (^{1}H NMR) and ^{13}C NMR spectra were recorded in CDCl$_3$ using Varian Mercury 300 MHz and 75 MHz spectrometers, respectively. The Fourier-transformed infrared data were obtained with a Varian FTS 800 spectrometer (Varian, Palo Alto, CA, USA) using a KBr pellet. High-resolution mass spectrometry (HRMS) was performed using a JEOL JMS-700 mass spectrometer (Jeol, München, Germany) under fast atom bombardment (FAB) conditions. An Elementar Vario EL instrument (Hanau, Germany) was used for the elemental analysis. The ultraviolet–visible (UV–vis) spectra were measured using a Shimadzu UV-1601 UV–vis spectrometer (Shimadzu, Duisburg, Germany). The molecular weights of the polymers were estimated using a Tosoh gel permeation

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chromatography system (Tosoh, Tokyo, Japan). Cyclic voltammetry was performed using a Bioanalytical Systems CV-50W voltammetric analyzer (Bioanalytical Systems, West Lafayette, IN, USA) at a potential scan rate of $50 \, mV \, s^{-1}$ in a 0.1-M solution of tetrabutylammonium hexaflurorophosphate (Bu_4NPF_6) in dichloromethane. The thermal analyses were conducted using a Mettler Toledo TGA/SDTA 851e analyzer (Mettler Toledo, Columbus, OH, USA).

Preparation of PDIs[10a]

Perylene-3,4,9,10-tetracarboxylic dianhydride (10.0 mmol, 3.92 g), 10-nonade-cylamine (25.0 mmol, 7.09 g) and 15 g imidazole were heated under a N_2 atmosphere at 180 °C for 3 h. The reaction mixture was cooled to room temperature and dispersed in 200 ml ethanol and 500 ml of 4 M HCl and stirred overnight. The resulting red sticky solid was filtered, dissolved in chloroform, dried over $MgSO_4$ and concentrated. The crude compound was purified using column chromatography with a chloroform eluent to produce a red solid, which was N,N′-di(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic bisimide (7.91 g, 86%). The characterizations of these PDIs are as follows:

PDI($R = C_9H_{19}$). IR (KBr): 2927, 2850, 1699, 1657, 1597, 1459, 1404, 1336, 1248, 956, 851, 809, 745, 623 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): 8.67 (m, 8H), 5.18 (m, 2H), 2.25 (m, 4H), 1.87 (m, 4H), 1.25 (m, 56H) 0.83 (t, 12H). HRMS (FAB +): m/z = 923.6663 [MH +] (Calcd.: 923.6665).

PDI($R = C_5H_{11}$). IR (KBr): 2927, 2851, 1700, 1660, 1597, 1459, 1400, 1240, 957, 851, 809, 745, 625 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): 8.67 (m, 8H), 5.18 (m, 2H), 2.22 (m, 4H), 1.85 (m, 4H), 1.25 (m, 32H) 0.81 (t, 12H). HRMS (FAB +): m/z = 699.4158 [MH +] (Calcd.: 699.4162).

PDI($R = 2,6$-diisopropyl). ^{1}H NMR (CDCl$_3$, 300 MHz): 8.80 (dd, 8H), 7.53 (d, 2H), 7.38 (m, 4H), 2.77 (m, 1H), 1.19 (d, 24H). HRMS (FAB +): m/z = 710.3218 [MH +] (Calcd.: 711.3223).

PDI($R = CH[CH_2O(C_2H_4O)_3CH_3]_2$). ^{1}H NMR (CDCl$_3$, 300 MHz): 8.61 (m, 8H), 5.72 (m, 2H), 4.19 (m, 4H), 3.98 (m, 4H), 3.78-3.40 (m, 60H). HRMS (FAB +): m/z = 1123.5210 [MH +] (Calcd.: 1123.5226).

Preparation of 4-alkyl-1,2,4-triazole-3,5-diones

The synthetic procedure for these compounds was obtained from the method found in the literature,[16] and their characterizations are as follows:

CPTAD. IR (KBr): 1920, 1895, 1790, 1770, 1706, 1662, 1638, 1530, 1406, 1184, 1156, 1092, 898, 747, 626, 570 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): 7.55 (d, 2H), 7.46 (d, 2H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 157.6, 139.6, 130.4, 128.2, 125.2. LCMS: m/z = 209.02 [M +] (Calcd.: 209.00).

BPTAD. IR (KBr): 1898, 1844, 1787, 1772, 1713, 1532, 1183, 1171, 1067, 1051, 897, 829, 738, 567 cm-1. ^{1}H NMR (CDCl$_3$, 300 MHz): 7.69 (d, 2H), 7.40 (d, 2H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 157.5, 133.4, 132.9, 125.4, 123.7. LCMS: m/z = 252.95 [M +] (Calcd.: 252.95).

CHTAD. IR (KBr): 2935, 2854, 1840, 1770, 1530, 1456, 1423, 1390, 1258, 1185, 1138, 895, 740, 559 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 3.93 (m, 1H), 2.20-1.55 (m, 6H), 1.55-1.20 (m, 4H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 159.2, 54.6, 29.4, 25.6, 24.8. LCMS: m/z = 181.05 [M +] (Calcd.: 181.09).

OCTAD. IR (KBr): 2940, 2850, 1840, 1775, 1530, 1423, 1390, 1258, 1240, 1186, 1140, 895, 560 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 3.64 (m, 2H), 1.75-1.40 (m, 2H), 1.28-1.00 (m, 10H), 0.81 (t, 3H). LCMS: m/z = 211.15 [M +] (Calcd.: 211.13).

Preparation of N-fused coronene octacarboxylic tetraimide: general coupling procedure

4-(p-Chlorophenyl)-1,2,4-triazole-3,5-dione (CPTAD; 15.0 mmol, 3.14 g) and p-chloranil (7.50 mmol, 1.84 g) were added to a solution of perylene diimide (PDI; 1.50 mmol, 1.38 g) in dried benzene (15 ml). The mixture was heated at 75 °C under a N_2 atmosphere for 7 days. The resulting mixture was concentrated, re-dissolved in n-hexane and filtered through sintered glass. The filtrate was evaporated to dryness and roughly purified using column chromatography, with chloroform and acetone/chloroform (1/10, v/v) as eluents. An isolated dark blue product was precipitated into methanol to give

pure FCTI-Cl (1.70 g, 85%). The characterization of this compound is as follows: IR (KBr): 3106, 2955, 2854, 1776, 1731, 1703, 1661, 1603, 1572, 1495, 1369, 1300, 1232, 1174, 829, 806, 774, 731 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.87 (m, 4H), 7.65 (d, 4H), 7.49 (d, 4H), 4.94 (m, 2H), 2.11 (m, 4H), 1.83 (m, 4H), 1.25 (m, 56H), 0.83 (t, 12H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 161.8, 157.4, 143.0, 135.5, 133.3, 129.9, 128.3, 127.9, 125.6, 124.0, 123.4, 116.3, 55.9, 32.2, 29.9, 29.8, 29.6, 27.3, 22.9, 14.4. UV–vis (CHCl$_3$): λ_{max} (ε, $lmol^{-1} \, cm^{-1}$) = 703 (15 200), 773 nm (18 800). HRMS (FAB +): m/z = 1337.6331 [MH +] (Calcd.: 1337.6337).

Other bis-adducts were similarly prepared, and their characterizations are as follows:

FCTI-Br. IR (KBr): 3106, 2955, 1776, 1727, 1704, 1603, 1464, 1408, 1170, 734, 698, 664, 626 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): 8.85 (m, 4H), 7.60 (m, 8H), 4.93 (m, 2H), 2.11 (m, 4H), 1.83 (m, 4H), 1.25 (m, 56H) 0.83 (t, 12H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 161.9, 158.8, 142.9, 133.4, 132.9, 128.7, 128.2, 125.7, 124.0, 123.6, 123.4, 116.3, 55.8, 32.2, 29.9, 29.8, 29.6, 27.3, 22.9, 14.4. UV–vis (CHCl$_3$): λ_{max} (ε, $lmol^{-1} \, cm^{-1}$) = 703 (15 300), 773 nm (18 800). HRMS (FAB +): m/z = 1425.5320 [MH +] (Calcd.: 1425.5327).

FCTI-Cy. IR (KBr): 3100, 2955, 2925, 2854, 1777, 1722, 1706, 1606, 1505, 1455, 1407, 1349, 735, 504 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): 8.80 (m, 4H), 5.00 (m, 2H), 4.14 (m, 2H) 2.32–2.01 (m, 8H), 2.00–1.69 (m, 14H), 1.25 (m, 62H) 0.86 (t, 12H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 161.9, 158.7, 144.1, 133.5, 125.9, 124.0, 123.2, 116.4, 55.5, 53.4, 32.2, 29.9, 29.8, 29.6, 29.1, 27.2, 26.0, 25.2, 22.9, 14.4. UV–vis (CHCl$_3$): λ_{max} (ε, $lmol^{-1} \, cm^{-1}$) = 719 (19 400), 792 nm (17 900). HRMS (FAB +): m/z = 1281.8052 [MH +] (Calcd.: 1281.8055).

FCTI-Oc. IR (KBr): 3100, 2955, 2920, 1770, 1730, 1706, 1611, 1500, 1454, 1411, 1350, 1120, 741, 511 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): 8.80 (m, 4H), 5.00 (m, 2H), 3.82 (m, 2H) 2.11 (m, 4H), 1.83 (m, 4H), 1.62 (m, 4H), 1.25 (m, 76H), 0.80 (m, 18H). UV–vis (CHCl$_3$): λ_{max} (ε, $lmol^{-1} \, cm^{-1}$) = 719 (19 300), 792 nm (18 000). HRMS (FAB +): m/z = 1341.8981 [MH +] (Calcd.: 1341.8994).

FCTI-11. IR (KBr): 3106, 2958, 2854, 1776, 1731, 1703, 1660, 1572, 1495, 1371, 1300, 1233, 1174, 825, 805, 774, 731 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 8.87 (m, 4H), 7.65 (d, 4H), 7.49 (d, 4H), 4.94 (m, 2H), 2.10 (m, 4H), 1.83 (m, 4H), 1.25 (m, 24H), 0.80 (t, 12H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 161.8, 157.3, 143.0, 135.3, 132.3, 129.8, 128.3, 127.9, 125.5, 124.1, 123.2, 116.2, 55.0, 32.0, 29.6, 27.3, 22.9, 14.0. UV–vis (CHCl$_3$): λ_{max} (ε, $lmol^{-1} \, cm^{-1}$) = 703 (15 000), 775 nm (18 300). HRMS (FAB +): m/z = 1113.3835 [MH +] (Calcd.: 1113.3823).

DPTI-Cl. IR (KBr): 3105, 2966, 2958, 2850, 1777, 1730, 1728, 1703, 1662, 1572, 1495, 1371, 1174, 801, 729 cm^{-1}. ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 9.21 (s, 4H), 7.59 (s, 6H), 7.60–7.44 (m, 2H), 7.38–7.19 (m, 4H), 2.62 (m, 2H), 1.16 (d, 24H). UV–vis (CHCl$_3$): λ_{max} (ε, $lmol^{-1} \, cm^{-1}$) = 700 (13 000), 771 nm (15 300). HRMS (FAB +): m/z = 1125.2888 [MH +] (Calcd.: 1125.2894).

Preparation of a diamine monomer

2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (3.0 mmol, 1.1 g), n-octyl alcohol (8.0 mmol, 1.3 ml) and triphenylphosphine (6.1 mmol, 1.6 g) were dissolved in anhydrous tetrahydrofuran (15 ml) under a N_2 atmosphere, and diethyl azodicarboxylate (1.6 mmol, 1.0 ml) was added dropwise over 30 min at 10 °C. After stirring for 10 h, the mixture was concentrated and mixed with diethyl ether (40 ml) to remove the insoluble phosphine oxide. The resulting ether solution was concentrated and purified using column chromatography with ethyl acetate and n-hexane (1/4, v/v) as the eluents to produce 2,2-bis(3-amino-4-n-octyloxyphenyl)hexafluoropropane (620 mg, 35%). The characterization of this compound is as follows: ^{1}H NMR (CDCl$_3$, 300 MHz): 6.91–6.62 (m, 6H), 4.05 (t, J = 6.3Hz, 4H), 3.8 (s, 4H), 1.88 (m, 4H), 1.80–1.25 (m, 20H), 0.99 (t, J = 6.9Hz, 6H). ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 147.1, 135.9, 126.1, 124.5 (q), 120.7, 117.2, 110.3, 68.4, 63.9 (m), 32.2, 29.6, 29.5, 29.5, 26.4, 22.9, 14.3. LCMS: m/z = 590.30 [M +] (Calcd.: 590.33).

Preparation of a polyimide (red-polyimide)

Perylene-3,4,9,10-tetracarboxylic dianhydride (0.10 mmol, 39 mg) and 2,2-bis(3-amino-4-n-octyloxyphenyl)hexafluoropropane (1.0 mmol, 591 mg) were placed in a round-bottom flask equipped with a refluxing condenser and charged with anhydrous m-cresol (4 ml) under a N_2 atmosphere. The mixture was heated for 4 h at 200 °C after adding isoquinoline (110 mg). 4,4'-oxydiphthalic anhydride (0.90 mmol, 279 mg) was added to the reaction mixture and further stirred for 24 h at 200 °C. The cooled mixture was precipitated into methanol, filtered and dried in a vacuum oven (70 °C, 12 h) to produce **red-polyimide** (0.71 g, 89%). The characterization of this compound is as follows: ^{1}H NMR (CDCl$_3$, 300 MHz): 8.75 (br, perylene Ar), 7.98 (d), 7.60–7.25 (m), 7.05 (d), 3.99 (m), 1.8–1.55 (m), 1.55–1.00 (m), 0.90 (t). See Supplementary Data for the detailed NMR spectrum. Gel permeation chromatography (tetrahydrofuran, polystyrene standard): number average molecular weight (Mn) = 8.3 kg mol^{-1}, Mw = 14.1 kg mol^{-1}. UV–vis (CHCl$_3$): λ_{max} = 458, 490, 526 nm. Anal. Calcd. for $(C_{55}H_{49}F_6N_2O_6)_{0.1}$ $(C_{47}H_{47}F_6N_2O_7)_{0.9}$: C, 65.74; H, 5.35; N, 3.21; O, 12.64. Found: C, 65.37; H, 5.71; N, 3.05; O, 12.81.

Preparation of green-polyimide

Red-polyimide (0.50 g), **CPTAD** (0.24 g) and p-chloranyl (0.14 mg) were placed in a round-bottom flask equipped with a refluxing condenser, and anhydrous benzene (8 ml) was added under a N_2 atmosphere. The red solution was heated for 6 days at 75 °C and a dark green color was observed. The cooled mixture was poured into methanol, filtered and dried in a vacuum oven (70 °C, 12H) to produce **green-polyimide** (0.54 g). The characterization of this compound is as follows: ^{1}H NMR (CDCl$_3$, 300 MHz): 9.25 (br, perylene Ar), 8.00 (d), 7.60–7.20 (m), 7.05 (d), 3.99 (m), 1.8–1.55 (m), 1.55–1.00 (m), 0.90 (t). (The detailed NMR spectrum is provided in the Supplementary Data.) Gel permission chromatography (tetrahydrofuran, polystyrene standard): Mn = 8.5 kg mol^{-1}, Mw = 14.3 kg mol^{-1}. UV–vis (CHCl$_3$): λ_{max} = 650, 709, 782 nm. Anal. Calcd. for $(C_{71}H_{53}Cl_2F_6N_8O_{10})_{0.1}(C_{47}H_{47}F_6N_2O_7)_{0.9}$: C, 64.79; H, 5.25; N, 3.98; O, 12.76. Found: C, 64.61; H, 5.47; N, 3.69; O, 12.93.

Solar cell fabrication and measurement

A bulk heterojunction solar cell was fabricated by first dissolving poly(3-hexylthiophene) and a bis-adduct (1/1 or 1/2, wt/wt) in a co-solvent of chloroform and toluene (1/1, v/v). This solution was spin-coated onto indium tin oxide-covered glass substrates that were previously coated with 40 nm of PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)). After drying the coated indium tin oxide, an Al top electrode (150 nm) was deposited in vacuo onto the organic layer using a shadow mask via thermal evaporation (base pressure $< 1.5 \times 10^{-8}$ Pa). The pixel size, as defined by the overlap of the indium tin oxide substrate and the Al back electrode, was 4 mm^2. Thermal annealing was performed at 80 °C (10 min) under a dry Ar atmosphere. The current–voltage of the solar cell was measured under simulated solar light illumination at an intensity of 100 mW cm^{-2} (AM 1.5) provided by a solar simulator (Orel 300 W). The electrical data were recorded using a Keithley 236 source-measure unit. The photocurrent action spectra were obtained by illuminating the samples with light from a 300 W Xenon lamp that was dispersed by a single-grating monochromator (DM151i, DongWoo Optron, Gwangju, South Korea). The film thickness was measured using a KLA Tencor Alpha-step IQ surface profilometer (KLA Tencor, Milpitas, CA, USA).

RESULTS AND DISCUSSION

Depending on the starting diene and dienophile, thermal cycloaddition is a good method for synthesizing fused cycles. Coronene can be obtained from the ring expansion of the double cycloaddition reaction between perylene and an alkyne.[4,5] This reaction is often limited to a perylene structure. Electron-withdrawing substituents on perylene require harsh reaction conditions for cycloaddition. For example, PDI shows very low conversion with malonic anhydride at 200 °C, and the successive reactions of the resulting mono-adduct does not occur for a bis-adduct.[4,5] A more reactive dienophile is needed for the formation of the bis-adduct. Soluble **PDI** has been derived from perylene tetracarboxylic dianhydride with a long alkyl chain swallowtail or a ring-distortion substituent, such as 2,6-diisopropyl phenyl.[17,18] 10-Aminononadecane reacted with perylene tetracarboxylic dianhydride to produce a **PDI** with two C19-alkyl groups. No adduct was detected when **PDI** was treated with propynyl benzoate in 1,2-dichlorobenzene under reflux. 1,2,4-Triazoline-3,5-dione was considered a strong dienophile, which produced a perylene adduct containing N-heterocycle. H Langhals et al.[12,13] reported the cycloaddition of **PDI** and 4-phenyl-1,2,4-triazole-3,5-dione, albeit in low yield. They improved the yield by using a 10-fold excess of dienophile and chloranyl, and isolated the mono-adduct and bis-adduct in 49% and 20% yield, respectively. The addition of chloranyl led to the oxidative re-aromatization of the adducts and shifted the reversible cycloaddition. The bis-adduct has an interesting structure and produces an N-heterocyclic analog of coronene, which would be generated through a ring-opening reaction,[19] as shown in Figure 1. Many attempts have been made to prepare the bis-adduct in a practical synthetic yield. The thermal cycloaddition of **PDI** and CPTAD was examined at different temperatures and quantities of oxidant. The results are summarized
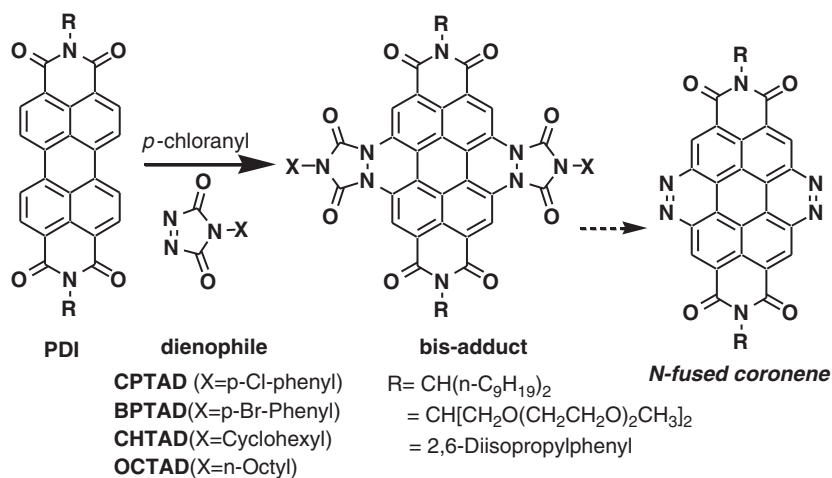

Figure 1 The cycloaddition of perylene diimide (**PDI**) and several dienophiles for N-fused coronene analogs.

Table 1 The optimized conditions for the formation of a bis-adduct of perylene diimide

Entry[a]	Chloranil equivalent	Solvent	Temperature (°C)	Run time day	Yield (%)[b]
1	0	Benzene	75	2	19
2	2	Benzene	75	2	26
3	5	Benzene	75	2	30
4	2	Toluene	110	2	7
5	5	Toluene	110	2	9
6	2	Xylene	140	2	Trace
7	5	Benzene	75	7	55(85)[c]

[a]The reaction was performed with perylene diimide (**PDI**; nonadecyl) and 5 equivalents **CPTAD** unless otherwise.
[b]Isolated yield of a bis-adduct **FCTI-Cl**.
[c]10 equivalents **CPTAD** was used.

Table 2 The synthetic results for the bis-adduct of perylene diimide with various substituents

Entry[a]	Substituent R	X	Dienophile	Bis-[b] adduct	Yield (%)[c]
1	CH(n-C$_9$H$_{19}$)$_2$	p-Cl-Ph	**CPTAD**	**FCTI-Cl**	85
2	CH(n-C$_9$H$_{19}$)$_2$	p-Br-Ph	**BPTAD**	**FCTI-Br**	86
3	CH(n-C$_9$H$_{19}$)$_2$	C$_6$H$_{11}$	**CHTAD**	**FCTI-Cy**	90
4	CH(n-C$_9$H$_{19}$)$_2$	n-C$_8$H$_{19}$	**OCTAD**	**FCTI-Oc**	92
5	CH(n-C$_5$H$_{11}$)$_2$	p-Cl-Ph	**CPTAD**	**FCTI-11**	79
6	2,6-diisopropyl phenyl	p-Cl-Ph	**CPTAD**	**DPTI-Cl**	78
7	CH[CH$_2$O(CH$_2$ -CH$_2$O)$_3$CH$_3$]$_2$	p-Cl-Ph	**CPTAD**	**EOTI-Cl**	74[d]

Abbreviation: CPTAD, 4-(p-Chlorophenyl)-1,2,4-triazole-3,5-dione.
[a]Each reaction was performed with dienophile (10 equivalents), oxidant (5 equivalents) and perylene diimide in benzene (75 °C) for 7 days.
[b]Abbreviated names of bis-adducts.
[c]The isolated yield of a bis-adduct.
[d]Very low solubility.

in Table 1. The reaction was performed under refluxing xylene for the favorable thermal aromatization of a nonaromatic intermediate. The reaction did not progress and the **PDI** was recovered. This was attributed to the thermal instability of **CPTAD**, which begins to decompose at temperatures lower than 80 °C, according to the thermogravimetric analysis (Supplementary Material). Using an excess of **CPTAD** compensated for the thermal cycloaddition reaction rate at lower temperatures. The cycloaddition required a long reaction time and was optimized at 75 °C. The reaction occurred without an additional oxidant in entry 1, where the initial adduct could be oxidized by the excess **CPTAD**. This was feasible because the **CPTAD** was prepared from the oxidation of a corresponding diazine and was reduced through hydrogenation.[16] **CPTAD** is unstable in the presence of moisture and heat and decomposes during the long cycloaddition period. Owing to these **CPTAD**-consumption pathways, an excess of **CPTAD** is essential for a better yield. The reaction yield increased until a fivefold excess of chloranil was used. Chloranil represses the loss of **CPTAD** as a competitive oxidant as well as by shifting the cycloaddition. The bis-adduct **FCTI-Cl** was isolated in 85% yield when the reaction was performed with 5- and 10-fold excesses of chloranil and **CPTAD**, respectively, for 7 days, as shown in entry 7 (Table 1). A mono-adduct[12,13] could be detected in small quantities during the reaction but disappeared by the end. Nitrogen substituents at the bay site of the mono-adduct provided electron density to the electron-deficient **PDI** and enhanced the reactivity of the mono-adduct, which led to the formation of a bis-adduct. Under the optimized conditions, the **PDI** coupling reaction occurred with various triazolediones dienophiles to afford each bis-adduct in high yield. Table 2 lists the synthetic results for a range of adducts. To some extent, the reaction yield correlates with the solubility of the **PDI** derivative. The less soluble **PDI** with 6-undecyl resulted in a lower yield than the **PDI** with nonadecyl, as shown in entry 5 in Table 2. **EOTI-Cl** and **DPTI-Cl** were isolated in yields of 78% and 74% yield, respectively, along with a small quantity of starting **PDI** and known materials. This might be due to the lower solubility of the initial nonaromatic intermediate, which may undergo retro-cyclization or decomposition in an unexpected manner. The polymerization of **DPTI-Cl** was attempted through an aryl–aryl coupling reaction. Most of the **PDI-Cl** was recovered when the **DPTI-Cl** was heated with an excess of copper in dimethylformamide under reflux. The palladium-catalyzed polymerization of **DPTI-Br** or **DPTI-Cl** failed to generate polymers under Stille's coupling conditions.[20] The focus of the present study then shifted to a polymer reaction in which a

perylene-involved polymer reacted with **CPTAD**. A copolyimide was developed from perylene tetracarboxylic dianhydride and a diamine.[21,22] For the soluble polyimide, the diamine was alkylated with an n-octyl group, and the perylene content was controlled using 4,4'-oxydiphthalic anhydride. The soluble **red-polyimide** contains 10 mol% perylene and a Mn of 8.3 kg mol^{-1}, as shown in Figure 2. When the **red-polyimide** was heated with **CPTAD** and chloranil in benzene at 75 °C, the solution color became dark green after 6 days and the **green-polyimide** was isolated. The perylene content of the polyimide was determined by ^{1}H NMR spectroscopy. When the eight perylene protons (H$_a$) were compared with two specific protons (H$_b$) from the 4,4'-oxydiphthalic anhydride unit in **red-polyimide**, the peak integration gave an ~4:9 ratio, indicating that there was 10 mol% of the perylene unit. The mole percentage was retained in the **green-polyimide**, with a H$_A$ and H$_B$ ratio of ~2:9. The cycloaddition of **CPTAD** apparently occurred on the perylene unit of **red-polyimide**. The chemical shifts of the aromatic protons of the polyimides were compared before and after the cycloaddition. A singlet peak for the **red-polyimide** at 8.7 p.p.m. was assigned to a perylene ring; this peak moved to 9.2 p.p.m. for the **green-polyimide** after cycloaddition. The relative peak integration of the perylene protons was reduced by 50% in the **green-polyimide**, as expected. The UV–vis absorption spectra of the polyimides explained the evident color change from the cycloaddition on a perylene unit (Figure 3). The characteristic absorption of the **PDI** below 550 nm disappeared and new absorption was observed at 600–850 nm after cycloaddition, yielding a bis-adduct **FCTI-Cl**. Similar absorption bands were observed in the spectrum for the **green-polyimide**, indicating the cycloaddition onto a perylene unit of the polyimide. In addition, a mono-adduct that appeared during cycloaddition showed a transient absorption range between the **PDI** and the bis-adduct. Table 3 lists the optical characterization of the prepared N-fused coronene derivatives. The optical band gap, which was calculated from the absorption edge of the film spectrum, was 1.3 eV. A low band gap is required for semiconductors,[8–11] near-infrared applications[12,13] and solar cells.[21,22]

The cyclic voltammetry analysis of **FCTI-Cl** determined that the lowest unoccupied molecular orbital and the highest occupied molecular orbital levels were 3.75 and 5.38 eV, respectively. The lowest unoccupied molecular orbital level is similar to that of phenyl-C61-
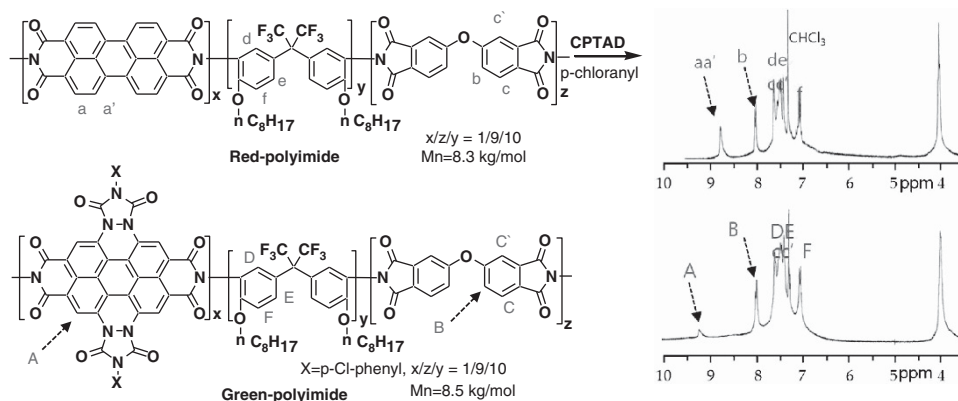
Figure 2 The cycloaddition of perylene-containing polyimide and the [1]H-nuclear magnetic resonance (^{1}H NMR; CDCl$_3$) analysis. A full color version of this figure is available at *Polymer Journal* online.
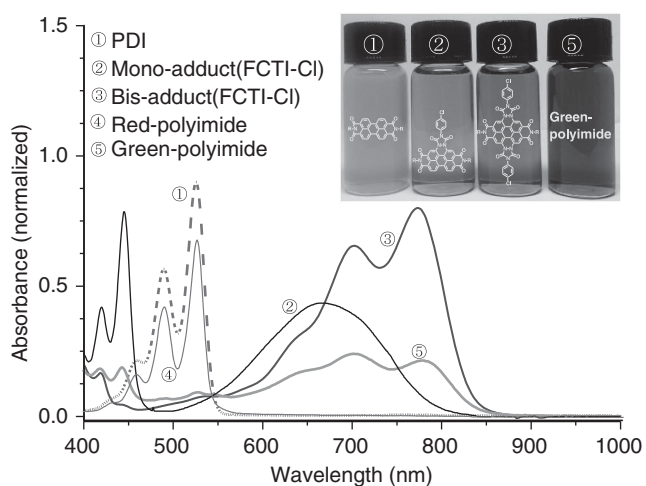

Figure 3 The ultraviolet–visible (UV–vis) absorption spectra of perylene diimide (**PDI**), mono- and bis-adducts, **red-polyimide** and **green-polyimide**. A full color version of this figure is available at *Polymer Journal* online.

Table 3 The optical properties of N-fused coronenes and polymers

Material	λ_{max}[a] (nm)	λ_{max} film (nm)	λ_{onset} film (nm)	E_g(optical)[b] (eV)
PDI	459(20)	472	594	2.09
	490(50)	497		
	525(88)	542		
FCTI-Cy	719(19)	772	959	1.29
	792(18)	874		
FCTI-Cl	703(15)	771	956	1.30
	773(19)	865		
FCTI-Br	703(15)	772	956	1.30
	773(19)	869		
Red-polyimide	458, 490	462, 492	578	2.15
	526	528		
Green-polyimide	650,709	725	930	1.33
	782	800		

Abbreviation: PDI, perylene diimide.
[a]Measured in chloroform, and parentheses indicate a molar absorption coefficient ($\varepsilon \ast 10^{-3}$, $l\,mol^{-1}\,cm^{-1}$).
[b]Optical band gap (E_g) = $1240/\lambda_{onset}$ from a film.

Table 4 The results of a solar cell using bis-adducts as an acceptor material

	FCTI-Cy	FCTI-Cl			FCTI-Cl/
Material	1/1	1/1	1/1(annealed)[a,b]	1/2	PCBM[c]
V_{oc} (V)	0.26	0.26	0.27	0.26	0.34
J_{sc} ($\mu A\,cm^{-2}$)	12.1	18.5	48.1	5.6	131
FF (%)[d]	18.8	24.5	26.1	25.9	17.1
PCE (10^{-3}%)[e]	0.6	1.2	3.4	0.4	7.6

Abbreviations: J_{sc}, current densities; V_{oc}, open-circuit voltage.
A bulk heterojunction solar cell was fabricated with a structure of the indium tin oxide (ITO)/ PEDOT:PSS (40 μm)/active layer(150 μm)/Al and measured under AM 1.5.
[a]Weight ratio of poly(3-hexylthiophene) (P3HT)/bis-adduct.
[b]Thermally annealed (10 min per 80 ºC).
[c]Blending ratio of P3HT/FCTI-Cl/PCBM (1/1/1 by weight).
[d]Fill factor.
[e]Power conversion efficiency.

butyric acid methyl ester (PCBM), which is a popular acceptor material in an organic solar cell. Table 4 summarizes the performance of the solar cells that used **FCTI-Cl** as an acceptor. A bulk heterojunction solar cell was fabricated with a composite of poly(3-hexylthiophene) and **FCTI-Cl**. The current densities (J_{sc}) of the devices were very low and therefore showed low conversion efficiencies. The efficiency was slightly enhanced with thermal passivation but was still low when compared with the known devices using poly(3-hexylthiophene)/PCBM.[21,22]

In conclusion, N-fused coronene octacarboxylic tetraimide derivatives were synthesized by thermal cycloaddition with high yields. The successive cycloaddition of 1,2,4-triazoline-3,5-dione occurred at both bay sites of PDI and primarily yielded a bis-adduct under the optimized reaction conditions. The reaction was performed on the perylene unit of perylene-containing polyimide and produced a polyimide with the characteristic near-infrared absorption.

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Supplementary Information accompanies the paper on Polymer Journal website (http://www.nature.com/pj)