Synthesis and Characterization of Highly Fluorescent Main-Chain Copolyimides Containing Perylene and Quinoxaline Units

Mukundan Thelakkat,* Peter Pösch, and Hans-Werner Schmidt

Makromolekulare Chemie I and Bayreuther Institut für Makromolekülforschung (BIMF),
Universität Bayreuth, D-95440 Bayreuth, Germany

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ABSTRACT: Two series of copolyimides, poly(quinoxaline perylene bisimide)s and poly(quinoxaline perylene bisimide ether)s, carrying quinoxaline units and varying amounts of substituted perylene bisimides in the main chain have been synthesized. The polymers were characterized by FT-IR, NMR, UV/vis, and fluorescence spectroscopy as well as GPC, DSC, and TGA measurements. They are highly soluble in usual solvents like $CHCl_3$, THF, etc., and form optically transparent films. The incorporation of varying amounts of perylene diimides with different substitution patterns allowed the control of fluorescence wavelength and intensity in solution and in thin films. The copolyimides with 1 mol % of perylene diimide content exhibit highest solid-state fluorescence. The observed intense fluorescence and a constant maximum wavelength of absorption in the solid state for copolymers containing up to 2.82 mol % perylene content indicate the absence of chromophore aggregation. Both types of copolymers are thermally stable up to 420 °C and exhibit glass transition temperatures in the range 225−270 °C. Blends of these perylene-containing polymers with hole transport molecules show complete photoluminescence quenching due to efficient electron transfer.

Introduction

Perylene imides represent a class of highly thermostable n-type semiconductors exhibiting relatively high electron affinity among large-band-gap materials. They have characteristic intense light absorption in the visible region. Moreover, these compounds exhibit intense fluorescence with quantum yield reaching up to 100% in solution.[1] The fluorescence emission can be tuned from blue to red by varying the substitution pattern of the perylene core.[2,3] The photocharge generation and electron transport properties of low molecular weight perylene imides have been successfully demonstrated by applying these materials in photovoltaics,[4−7] light-emitting diodes,[8,9] xerography,[10] and field-effect transistors.[11] The basic property of electron transfer required for many of these electrooptical applications can be studied by fluorescence (FL) spectroscopy as well as spectroelectrochemistry.[12]

Most of the studied perylene imides are insoluble, and therefore the preparation of thin layers is carried out by the vapor deposition method. The alternative method of blending low molecular weight perylene imides with polymers to prepare smooth films has the inherent problem of phase separation. On the other hand, soluble low molecular perylene imide dyes can be obtained by introducing long and bulky substituents at 1,6,7,12 "bay positions" and/or at the imide nitrogen atoms. In an expanding field of organic electrooptic devices which utilize polymers as active materials, it is worthwhile to design soluble and film-forming polymers with enhanced electron transport property and fluorescence behavior. The synthesis and studies of a few soluble polyimides containing substituted perylene imide units[2,13] as well as unsubstituted perylene bisimide units[14,15] have been reported. The majority of these perylene-containing polymers exhibit strong fluorescence in solution whereas only weak emission is observed in the solid state. This is due to the high content of perylene chromophore (about 50 mol %) which leads to FL quenching through aggregation.[2,15]

Recently, we have shown that information regarding vibrational energy transfer in perylene imide polymers can be elucidated using two-pulse excitation fluorescence measurements on side-chain perylene polymers.[16] For the purpose of carrying out fluorescence spectroscopy measurements, the design of well-defined multichromophore molecules carrying perylene imides and perylene imide-labeled copolymer are also reported in the literature.[17,18]

The intensity and quantum yield of fluorescence of perylene imide polymers can be varied by incorporating different amounts of the active fluorescent moiety by copolymerization. In this way soluble polymers exhibiting high fluorescence can be prepared.[19] The intensity of fluorescence achieved is high due to an apparent dilution of the perylene chromophore in the copolymer chain, which in turn suppresses any fluorescence quenching effects. This allows the study of basic phenomena of charge generation and charge transfer in thin and stable films. To compensate the dilution effect in electron transport property due to copolymerization, we have incorporated electron transporting quinoxaline units in the main chain. We prepared two series of main-chain perylene imide copolymers, poly(quinoxaline perylene bisimide)s **4a−e** and poly(quinoxaline perylene bisimide ether)s **8a,b**, containing different amounts of perylene dye, The poly(quinoxaline perylene bisimide)s **4a−e** contain tetraphenoxy-substituted perylene diimides incorporated into polymer main chain through imide linkages, whereas in the poly(quinoxaline perylene bisimide ether)s **8a,b** the perylene diimide units are connected through ether linkages at 1,7 bay-positions via polycondensation. This should lead to different degrees of packing of the perylene group, thus influencing the fluorescence quantum yield in the two types of

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* To whom correspondence should be addressed. E-mail mukundan.thelakkat@uni-bayreuth.de.

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polymers. This paper reports the synthesis, characterization, and study of thermal and optical properties of these two series of copolymers in solution and in thin films.

Experimental Section

Materials. All solvents were dried and freshly distilled according to common methods of purification.[20] 1,6,7,12-Tetraphenoxy-3,4:9,10-perylenetetracarboxylic acid dianhydride (**1**) was synthesized from 1,6,7,12-tetrachloro-3,4:9,10-perylenetetracarboxylic acid dianhydride and phenol as described in the literature.[2] 1,6,7,12-Tetrachloro-3,4:9,10-perylenetetracarboxylic acid dianhydride was provided as reagent grade by BASF-AG. The comonomer diamine **2**, 4,4′-bis[6-(*p*-aminophenoxy)-3-phenyl-2-quinoxalyl]phenyl ether, was kindly provided as reagent grade by Prof. Rusanow, University of Moscow. The monomer **5** was synthesized as described in the following from 1,7-dibromo-*N*,*N*′-bis(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxylic acid diimide (BASF-AG) after purification by column chromatography (silica gel, *n*-hexane/diethyl ether = 1:2 by volume). 4,4′-(Hexafluoroisopropylidene)diphthalic anhydride (**3**, Aldrich) was sublimed under reduced pressure, and 2,2-bis(4-hydroxyphenyl)perfluoropropane (**6**, Aldrich) was first recrystallized from a toluene/ethyl acetate/*n*-hexane (19:1:4) solvent mixture and finally sublimed under reduced pressure before use. The purity of all the monomers was controlled by TLC, and the samples were freeze-dried to remove any moisture before use.

Monomer Synthesis. *1,6,7,12-Tetraphenoxy-3,4:9,10-perylenetetracarboxylic acid dianhydride* (**1**) was synthesized from 1,6,7,12-tetrachloro-3,4:9,10-perylenetetracarboxylic acid dianhydride and phenol as described in the literature,[2] and the tetracarboxylic acid formed is dissolved in an alcoholic sodium hydroxide solution (5% w/w) and reprecipitated by adding into diluted hydrochloric acid. Finally, it was dried in a vacuum at 70 °C to convert it into anhydride. Yield: 56%. ^{1}H NMR (250 MHz, CDCl$_3$): δ [ppm] = 8.1 (4H, s), 7.2 (12H, m), 6.8 (4H, d). FT-IR (KBr pellet): $\tilde{\nu}$ [cm^{-1}] = 3068, 2964, 2930, 2870, 1784, 1748, 1714, 1677, 1588, 1488, 1388, 1259, 1196, 840, 749, 692, 547. MS-EI: m/z = 760 [M$^{•+}$].

1,7-Bis[2-(4-hydroxyphenyl)perfluoropropylphenoxy]-N,N′-bis(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxylic diimide (**5**). 0.30 g (0.34 mmol) of 1,7-dibromo-*N*,*N*′-bis(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxylic diimide, 1.20 g (3.57 mmol) of 2,2-bis(4-hydroxyphenyl)perfluoropropane (**6**), 0.76 g (5.5 mmol) of K$_2$CO$_3$, and 30 mL of NMP were taken in a Schlenk flask, flushed with argon, and heated at 90 °C for 3 h. After cooling to room temperature NMP was removed by vacuum distillation, 50 mL of CHCl$_3$ was added to the black residue and stirred, and inorganic salts were filtered off. After removing the solvent the crude product (yield 0.27 g = 0.20 mmol, 59%) was purified by column chromatography (silica gel, ethyl acetate/cyclohexane = 1:2) and freeze-dried from benzene to give a bright red powder. ^{1}H NMR (250 MHz, CDCl$_3$): δ [ppm] = 9.5 (2H, d), 8.7 (2H, d), 8.4 (2H, s), 7.0−7.4 (18H, m), 6.7 (4H, d), 5.4 (2H, s), 2.6 (4H, m), 1.1 (24H, d). FT-IR (KBr pellet): $\tilde{\nu}$ [cm^{-1}] = 3434, 2967, 2933, 2873, 1710, 1663, 1596, 1508, 1407, 1340, 1258, 1208, 1174, 835. MS-EI: m/z = 1379 [M$^{•+}$].

4,4′-Bis[4-(7-fluoro-3-phenyl)-2-quinoxalyl])phenyl ether (**7**). 2.17 g (5.0 mmol) of 4,4′-di(benzilyl)phenyl ether, 1.44 g (11.2 mmol) of 1,2-diamino-4-fluorobenzene, 40 mL of CHCl$_3$, and 0.25 mL of trifluoroacetic acid were refluxed under argon atmosphere for 3 h. The mixture was cooled to room temperature, diluted with 20 mL of CHCl$_3$, and washed twice with diluted hydrochloric acid (5%) and finally with water. The organic phase was dried over MgSO$_4$, the solvent was evaporated, and the crude product was first recrystallized from an ethanol/CHCl$_3$ mixture (9:1) and then passed over a silica gel column (ethyl acetate/cyclohexane = 1:2). Finally, the product was freeze-dried from benzene to yield 2.61 g (4.3 mmol, 85%) of white powder which is an isomeric mixture. ^{1}H NMR (250 MHz, CDCl$_3$): δ [ppm] = 8.16 (2H, dd), 7.79 (2H, m), 7.60−7.55 (10H, m), 7.42−7.34 (6H, m), 6.99 (4H, d). FT-IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 3060, 1621, 1596, 1503, 1482, 1345, 1240, 1207, 835, 697. MS-EI: m/z = 614 [M$^{•+}$].

1,6,7,12-Tetraphenoxy-N,N′-bis(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxylic diimide (**9**) was synthesized from **1** according to a similar procedure published earlier.[2,23] 2.57 g (14.5 mmol) of 2,6-diisopropylaniline and 274 mg (1.5 mmol) of anhydrous zinc acetate were added to a solution of 1.10 g (1.45 mmol) of 1,6,7,12-tetraphenoxy-3,4:9,10-perylenetetracarboxylic acid dianhydride (**1**) in 20 mL of quinoline. The mixture was stirred at 210 °C for 14 h under argon atmosphere. After cooling to room temperature the mixture was added to 400 mL of methanol/10% hydrochloric acid (v:v = 2:1). The solid precipitated was filtered off, stirred in 100 mL of cold sodium carbonate solution (10%) for 2 h, filtered again, and washed with water until the filtrate is colorless and nonfluorescent. The solid was dried under vacuum at 80 °C for 16 h to obtain 1.24 g of crude **9** (79% yield). The dark red powder was further purified by flash chromatography over silica gel with toluene/ethyl acetate (5:1) as eluent. ^{1}H NMR (250 MHz, CDCl$_3$): δ [ppm] = 8.26 (4H, s), 7.42−7.39 (2H, t), 7.30−7.24 (12H, m), 7.13−7.07 (4H, m), 6.90 (8H, d), 2.73−2.67 (4H, m), 1.12 (24H, d). FT-IR (KBr): $\tilde{\nu}$ [cm^{-1}] = 2960, 1706, 1674, 1586, 1507, 1487, 1384, 1341, 1285, 1198, 875, 751, 691. MS-EI: m/z = 1079 [M$^{•+}$].

Polymer Synthesis. *Poly(quinoxaline perylene bisimide)s* (**4a**−**e**). Polymer **4a** contains no perylene moiety, whereas polymers **4b**−**e** have different amounts of incorporated perylene.

4a: In a dried Schlenk flask 0.726 g (0.916 mmol) of **2**, 0.404 g (0.910 mmol) of **3**, 15 mL of *m*-cresol, and 0.5 mL of isoquinoline were added and flushed with argon. The flask was sealed with a solvent-resistant septum and heated to 80 °C (outer temperature) for 24 h. Then the temperature was raised to 210 °C for another 12 h, during which time a gentle argon steam was bubbled through the reaction mixture to remove the condensed water. The highly viscous polymer solution was cooled to room temperature, diluted with 40 mL of *m*-cresol, precipitated out of acetone, and filtered off. For further purification the polymer was dissolved in 50 mL of CHCl$_3$, reprecipitated in acetone, dried in a vacuum at 90 °C, and extracted with acetone for 3 days. Reprecipitation was repeated twice. The yield of the nearly colorless polymer was almost quantitative. ^{1}H NMR (250 MHz, CDCl$_3$): δ [ppm] = 8.2 (2H, d), 8.1 (2H, d), 8.0 (2H, s), 7.9 (2H, d), 7.6−7.2 (22H, m), 7.0−6.9 (8H, m) (no resonance signals from the perylene core were detected). FT-IR (film): $\tilde{\nu}$ [cm^{-1}] = 3065, 1785, 1731, 1597, 1507, 1480, 1373, 1347, 1236, 1211, 1170, 832, 723.

4b−**e**: As an example for the general three-step procedure for the preparation of perylene-containing polymers **4b**−**e**, the synthesis of polymer **4b** is given. The other copolymers of this series are accessible by varying the amounts of monomers. In a dried Schlenk flask 0.007 g (0.009 mmol) of **1**, 1.403 g (1.769 mmol) of **2**, 20 mL of *m*-cresol, and 0.5 mL of isoquinoline were added and flushed with argon. The flask was sealed with a solvent-resistant septum and heated to 210 °C (outer temperature) for 4 h. After cooling to room temperature, 0.782 g (1.761 mmol) of **3** was added to the mixture, the flask again flushed with argon, and sealed with the septum. After heating at 80 °C for 24 h the temperature was raised to 210 °C for another 12 h, during which time a gentle argon steam was bubbled through the reaction mixture to remove the condensed water. The green highly viscous polymer solution was cooled to room temperature, diluted with 40 mL of *m*-cresol, precipitated out of acetone, and filtered off. For further purification the pale-violet polymer was dissolved in 50 mL of CHCl$_3$, reprecipitated in acetone, dried in a vacuum at 90 °C, and extracted with acetone for 3 days. Reprecipitation was repeated until acetone was not colored by the perylene dye any longer.

The yields for these polycondensation reactions were in all cases almost quantitative; the color of resulting polymer flakes depends on the chromophore amount and varied from dark violet to bright pink.

4b: ^{1}H NMR (250 MHz, CDCl$_3$): δ [ppm] = 8.2 (2H, d), 8.1 (2H, d), 8.0 (2H, s), 7.9 (2H, d), 7.6−7.2 (22H, m), 7.0−6.9 (8H, m) (no resonance signals from the perylene core were detected).

FT-IR (film): $\tilde{\nu}$ [cm^{-1}] = 3067, 1785, 1731, 1597, 1508, 1480, 1376, 1346, 1236, 1209, 1169, 833, 721.

4c: 0.012 g (0.016 mmol) of **1**, 1.245 g (1.567 mmol) of **2**, 20 mL of *m*-cresol, 0.5 mL of isoquinoline, and 0.690 g (1.552 mmol) of **3** were reacted together as described above.

^{1}H NMR (250 MHz, CDCl$_3$): δ [ppm] = 8.2 (2H, d), 8.1 (2H, d), 8.0 (2H, s), 7.9 (2H, d), 7.6−7.2 (22H, m), 7.0−6.9 (8H, m) (no resonance signals from the perylene core were detected). FT-IR (film): $\tilde{\nu}$ [cm^{-1}] = 3066, 1787, 1725, 1595, 1503, 1479, 1369, 1348, 1234, 1211, 1171, 830, 721.

4d: 0.023 g (0.030 mmol) of **1**, 1.192 g (1.504 mmol) of **2**, 20 mL of *m*-cresol, 0.5 mL of isoquinoline, and 0.656 g (1.476 mmol) of **3** were reacted together as described above.

^{1}H NMR (250 MHz, CDCl$_3$): δ [ppm] = 8.2 (2H, d), 8.1 (2H, d), 8.0 (2H, s), 7.9 (2H, d), 7.6−7.2 (22H, m), 7.0−6.9 (8H, m) (no resonance signals from the perylene core were detected). FT-IR (film): $\tilde{\nu}$ [cm^{-1}] = 3064, 1786, 1725, 1595, 1502, 1480, 1369, 1344, 1236, 1210, 1170, 831, 719.

4e: 0.054 g (0.071 mmol) of **1**, 1.108 g (1.397 mmol) of **2**, 20 mL of *m*-cresol, 0.5 mL of isoquinoline, and 0.589 g (1.325 mmol) of **3** were reacted together as described above.

^{1}H NMR (250 MHz, CDCl$_3$): δ [ppm] = 8.2 (2H, d), 8.1 (2H, d), 8.0 (2H, s), 7.9 (2H, d), 7.6−7.2 (22H, m), 7.0−6.9 (8H, m) (no resonance signals from the perylene core were detected). FT-IR (film): $\tilde{\nu}$ [cm^{-1}] = 3063, 1786, 1730, 1597, 1506, 1479, 1373, 1345, 1236, 1210, 1170, 832, 722.

Poly(quinoxaline perylene bisimide ether)s (**8a,b**). As an example for the general procedure the synthesis of polymer **8a** is given. The other copolymer **8b** is accessible by varying the amounts of monomers. 0.023 g (0.017 mmol) of **5**, 1.015 g (1.652 mmol) of **7**, 0.550 g (1.635 mmol) of **6,** and 0.28 g (2.0 mmol) of K$_2$CO$_3$ were weighed into a completely argon-flushed Dean−Stark apparatus. 15 mL of NMP and 30 mL of toluene (both degassed by ultrasonics) were added, and the mixture was heated to 160 °C. This temperature was kept for about 2−3 h until all toluene was collected in the Dean−Stark trap. The color of the solution changed from red to green and finally to dark blue. To complete the reaction, the mixture was stirred for another 2 h at 190 °C and then cooled to room temperature, and the reaction was stopped by adding 2 mL of glacial acetic acid. Inorganic salts were filtered off, the polymer was precipitated out of acetone, and the crude product (yield 1.1 g, 99%) was stirred in water at 80 °C overnight. Repeated reprecipitation from CHCl$_3$ solution into acetone and extraction with hot ethanol yielded an orange-colored and filamentous polymer.

8a: ^{1}H NMR (250 MHz, CDCl$_3$): δ [ppm] = 8.2 (2H, d), 7.7−7.6 (4H, m), 7.5−7.2 (18H, m), 7.1 (4H, d), 6.9 (4H, m). FT-IR (KBr pellet): $\tilde{\nu}$ [cm^{-1}] = 3065, 3015, 1602, 1507, 1480, 1345, 1241, 1201, 1178, 965, 831, 754, 700.

8b: 0.034 g (0.025 mmol) of **5**, 0.769 g (1.251 mmol) of **7**, 0.412 g (1.226 mmol) of **6**, and 0.28 g (2.0 mmol) of K$_2$CO$_3$ were reacted as above. ^{1}H NMR (250 MHz, CDCl$_3$): δ [ppm] = 8.2 (2H, d), 7.7−7.6 (4H, m), 7.5−7.2 (18H, m), 7.1 (4H, d), 6.9 (4H, m). FT-IR (KBr pellet): $\tilde{\nu}$ [cm^{-1}] = 3067, 3014, 1603, 1505, 1479, 1346, 1241, 1205, 1175, 968, 832, 758, 697.

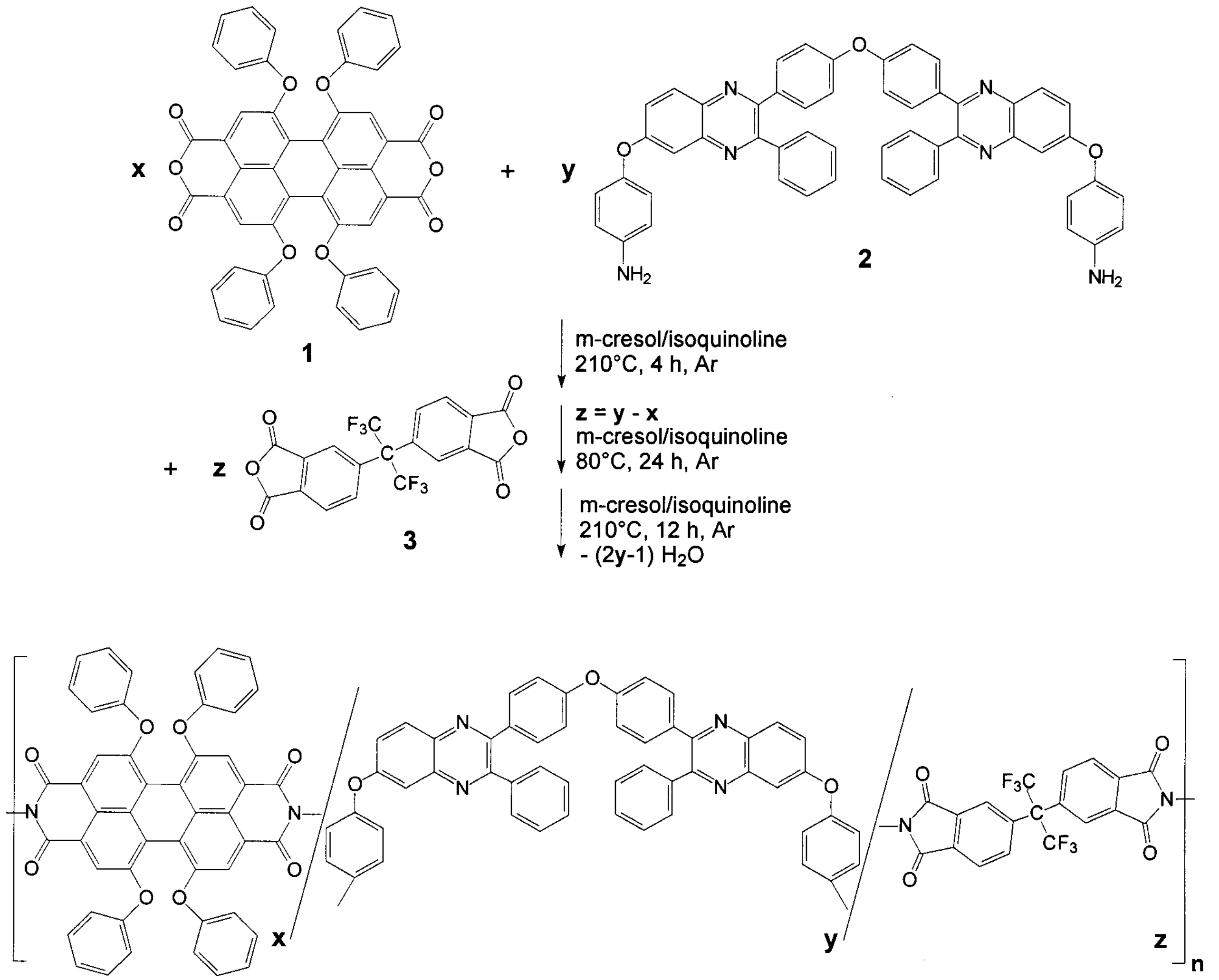
Instrumentation and Measurements. ^{1}H NMR: Bruker AC 250 (250 MHz). FT-IR: BioRad Digilab FTS-40. GPC: Waters 510 (UV and RI detector, PS standards, eluent THF). DSC: Perkin-Elmer DSC 7 (heating rate 10 K/min, N$_2$ purged). UV/vis: Hitachi U-3000 (films on quartz substrate). Fluorescence: Shimadzu RF 5301 PC (films on quartz substrate). TGA: Netzsch STA 409C (heating rate 10 K/min, N$_2$ atmosphere). MS-EI (70 eV): Finnigan MAT 8500 with Varian MAT 112 spectrometer.

Results and Discussion

An efficient way of incorporating differently substituted perylene diimide cores through covalent linkages into a main-chain polymer resulted in highly fluorescent and soluble copolymers. The dilution effect of the chromophore achieved by copolymerization is exploited here in the synthesis to obtain strong solid-state fluorescence in poly(quinoxaline perylene bisimide)s (**4a**−**e**) and poly(quinoxaline perylene bisimide ether)s (**8a,b**). On the one hand, the introduction of electron transporting quinoxaline moieties as comonomer prevents the fluorescence quenching due to aggregation of the perylene core, and on the other hand, it augments the charge transport properties.

The scheme of synthesis shown in Figure 1 describes the preparation of five different copolymers **4a**−**e** with varying mol % of perylene diimide chromophore (from 0 up to 2.65 mol % of weighed monomer **1**). The molar amount of diamine **2** was kept constant (50 mol %), and the amounts of the perylene dianhydride **1** and comonomer **3** were varied, keeping the total amount of both anhydrides equal to that of the diamine. The poly(quinoxaline imide) **4a** does not contain any perylene and serves the purpose of comparison as homopolymer with electron transport properties. The synthesis of the copolymers **4b**−**e** was carried out in a stepwise manner, taking into account the lower reactivity of the six-ring perylene dianhydride monomer **1** compared to the five-ring dianhydride monomer **3**. First, the whole of monomer **1** (0.25−2.65 mol %) was allowed to react with the diamine **2** (50 mol %) in *m*-cresol in the presence of isoquinoline at 210 °C to obtain a mixture of unreacted diamine **2** and amine-terminated species with incorporated perylene. In a second step, the more reactive monomer **3** was added, and the reaction was carried out at a lower temperature with an aim of obtaining soluble and high molecular weight poly(amic acid)s. In a final step these poly(amic acid)s were imidized by elimination of water via purging dry argon through the reaction mixture kept at a temperature of 210 °C. This method of synthesis proved to be an elegant way to obtain high molecular weight copolymers with almost the same amounts of incorporated perylene as taken in the reaction mixture. The conventional way of copolymerization by adding all the comonomers together at a time did not lead to the series of copolymers with exact amounts of perylene content and desired dilution effect. In polymers **4a**−**e** the completion of imidization is indicated by the absence of O−H-vibration band at about 3000 cm^{-1} and the C═O vibration band at 1670 cm^{-1} of poly(amic acid) as well as the C═O vibration band of the anhydride at 1850 cm^{-1}. Moreover, two new bands at 1787 ± 2 and 1728 ± 2 cm^{-1} due to the imide C═O stretching vibration are observed in the final polymers in addition to the typical C−N stretching at 1371 ± 2 cm^{-1}.

The poly(quinoxaline perylene bisimide ether)s **8a,b** were synthesized according to the scheme shown in Figure 2 using the method of activated nucleophilic aromatic substitution by reacting 0.5 and 1.0 mol % of perylene diimide diol **5** and comonomer bisphenol **6** (49.5 and 49 mol %) with π-electron-deficient difluoroquinoxaline derivative **7**.[21,22] The details of synthesis of monomers **5** and **7** are given in the experimental part. The functionalization of the perylene monomer **5** with the bulky perfluoropropyl phenoxy groups guarantees solubility and similar reactivity as the comonomer 2,2-bis(4-hydroxyphenyl)perfluoropropane (**6**). During the polycondensation, the reactivity of the carbonyl group in perylene diimide diol **5** toward the phenolate is sterically hindered due to the presence of bulky isopropyl substituents at the ortho position to the imide group, and this disfavors possible side reactions. The fact that the difluoroquinoxaline monomer **7** exists as an isomeric



4a-e

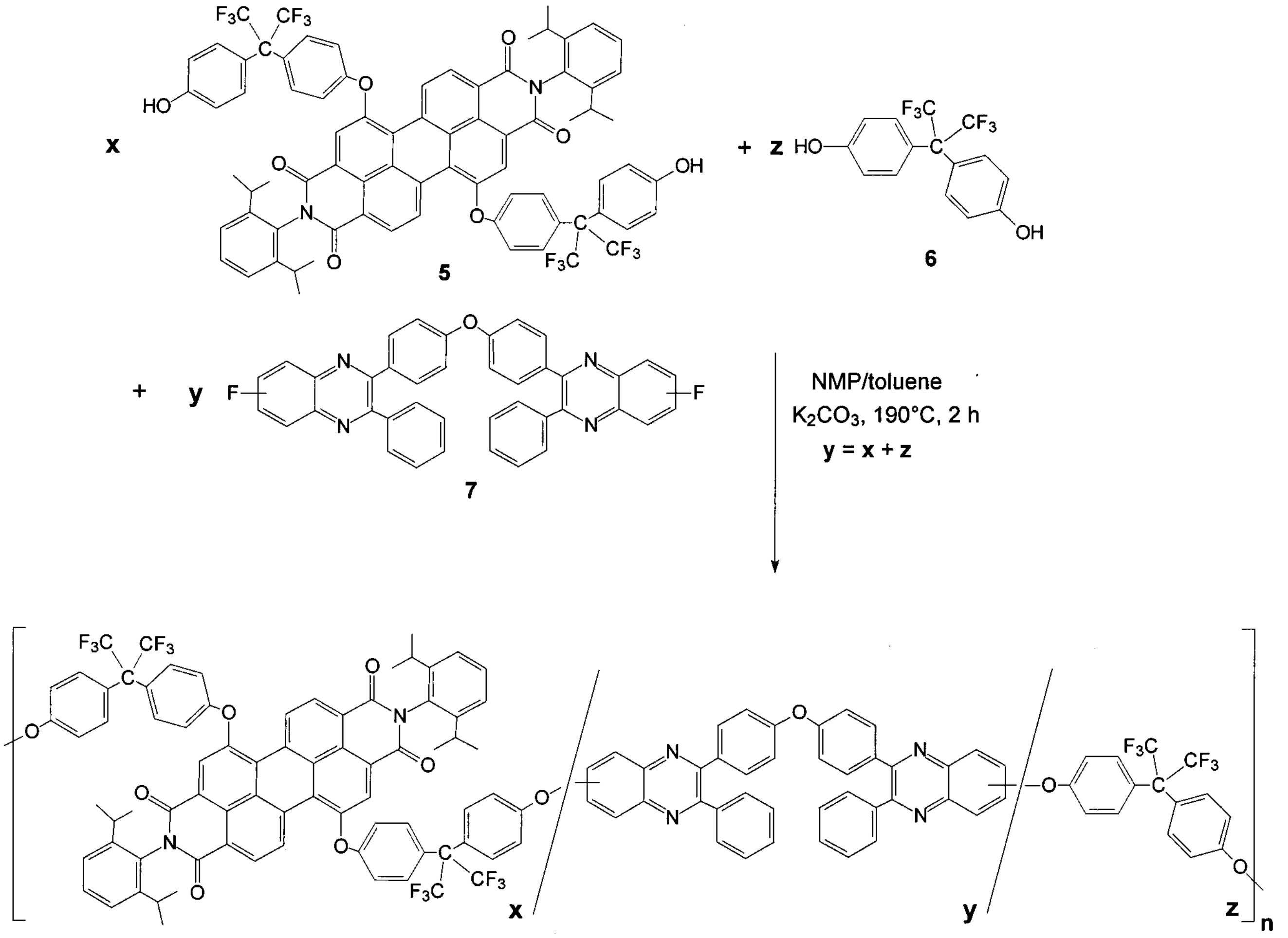
Figure 1. Scheme of synthesis of poly(quinoxaline perylene bisimide)s **4a**−**e** with varying amounts of perylene chromophore (*x* varies from 0 to 2.65 mol %, *y* is kept at 50 mol %, and *z* varies from 50 to 47.35 mol % as weighed amounts of respective monomers).

mixture contributes to enhanced solubility of the resulting polymers. In the case of **8a,b** the C−F vibration band of the monomer **7** at about 1160 cm^{-1} disappears, and a strong vibration band due to the C−O−C group at 1240 cm^{-1}originates in the polymer.

Determination of Incorporated Perylene Content in Copolymers from UV/vis Absorption Data. The usual method for determining the composition of a copolymer by NMR measurements could not be adopted here due to the extremely small amounts of incorporated perylene comonomers **1** and **5** (less than 2.65 mol %). Therefore, to determine the amount of incorporated perylene chromophores in both types of polymers quantitatively, we adopted the extinction coefficient (from UV−vis spectroscopy measurements) correlation of model compounds with those of polymers as reported in the literature.[18] For this purpose, we synthesized 1,6,7,12-tetraphenoxy-*N*,*N*′-bis(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxylic diimide (**9**) as model compound for the polymers **4a**−**e**. The monomer 1,7-bis[2-(4-hydroxyphenyl)perfluoropropylphenoxy]-*N*,*N*′-bis(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxylic diimide (**5**) was used as model compound for polymers **8a**−**b** (see Figure 3). The model compounds **9** and **5** have a similar substitution pattern as the parent polymers, poly(quinoxaline perylene bisimide)s **4a**−**e** and poly(quinoxaline perylene bisimide ether)s **8a**−**b**, respectively. In both cases, the optical density at the absorption maximum (A_{max}) was plotted vs concentration (c in mol L^{-1}) to obtain the extinction coefficient (ϵ_{max} in L mol^{-1} cm^{-1}) from the slope of the linear function, $\epsilon_{max} = A_{max}/cl$, where l is the path length (cm). The mole fractions (y) of incorporated perylene chromophore in the polymers were determined from the ratio of extinction coefficients for the polymer, $\epsilon_{p,max}$, and that for the corresponding model compound, $\epsilon_{m,max}$, from the equation $y = \epsilon_{p,max}/\epsilon_{m,max}$.

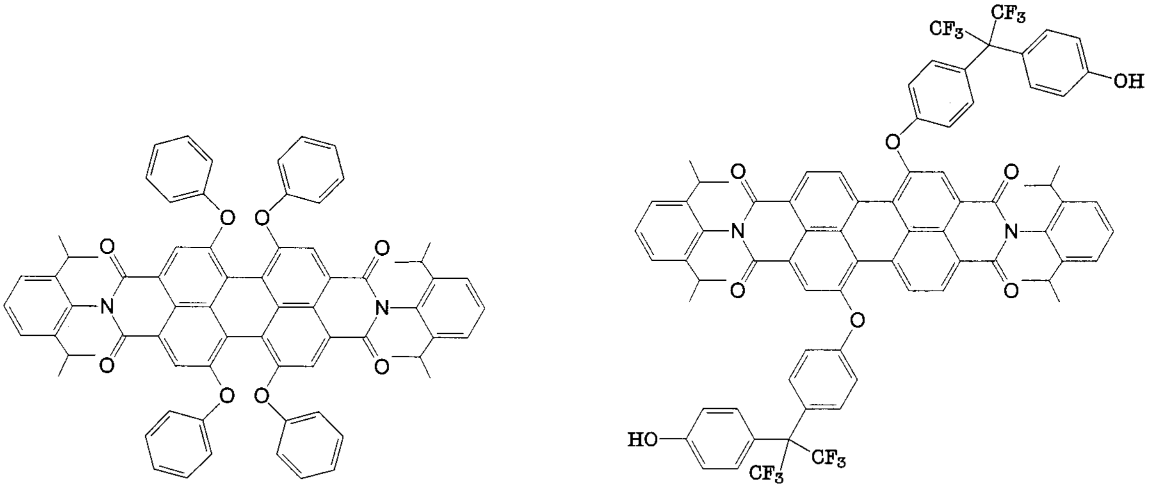
In the case of poly(quinoxaline perylene bisimide)s **4b**−**d** the amounts of covalently bound chromophore obtained from UV/vis spectroscopy are 0.32, 0.56, 1.15, and 2.82 mol %, respectively. For the polymers **8a** and **8b** the calculated amounts of bound chromophore units are 0.20 and 0.43 mol %, respectively (Table 1). It can be seen that the stepwise polycondensation used for the preparation of **4b**−**d** results in the incorporation of higher amounts of perylene units in a varying manner and in good agreement with the weighed amounts. In the case of polymers **8a** and **8b** about half of the weighed amounts are covalently fixed in the polymer main chain.

All the copolymers presented here show appreciably high solubility (>10 mg polymer in 1 g solution) in solvents like $CHCl_3$, THF, cyclohexanone, etc., and form



8a-b

Figure 2. Scheme of synthesis of poly(quinoxaline perylene bisimide ether)s **8a,b** with varying amounts of perylene chromophore ($x = 0.5$ mol % and $z = 49.5$ mol % for **8a**; $x = 1.0$ mol % and $z = 49.0$ mol % for **8b**; y is kept at 50 mol % as weighed amounts of respective monomers).



9 **5**

Figure 3. Chemical structures of the model perylene chromophores 1,6,7,12-tetraphenoxy-*N*,*N*′-bis(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxylic diimide (**9**) and 1,7-bis[2-(4-hydroxyphenyl)perfluoropropyl phenoxy]-*N*,*N*′-bis(2,6-diisopropylphenyl)-3,4:9,10-perylenetetracarboxylic diimide (**5**) (ϵ_{max} for **9** = 47 880 at 576 nm in $CHCl_3$; ϵ_{max} for **5** = 45 570 at 531 nm in $CHCl_3$).

optically transparent and stable films from solution. The chemical structures of the polymers were characterized by FT-IR and ^1H NMR spectroscopy measurements.

The number-average molecular weights as determined from size exclusion chromatography (GPC: polystyrene standards, THF as eluent) are in the range 18 000–29 000 g/mol. The GPC eluogramms show the characteristic broad molecular weight distribution for polycondensates with polydispersity of about 2.0–2.5. The GPC data and the thermal properties of the

Table 1. GPC, DSC, and TGA Data for the Polymers 4a–e and 8a,b

copolymer	**4a**	**4b**	**4c**	**4d**	**4e**	**8a**	**8b**
x^a [mol %]	0	0.25	0.5	1.0	2.65	0.5	1.0
x^b(calcd) [mol %]		0.32	0.56	1.15	2.82	0.20	0.43
$M_n{}^c$ [g/mol]	1.8×10^4	2.0×10^4	2.6×10^4	2.2×10^4	2.2×10^4	2.9×10^4	2.5×10^4
$M_w{}^c$ [g/mol]	4.0×10^4	4.3×10^4	6.0×10^4	5.5×10^4	5.6×10^4	5.7×10^4	4.8×10^4
M_w/M_n	2.2	2.1	2.3	2.5	2.6	2.0	1.9
$T_g{}^d$ [°C]	267	266	270	269	269	225	224
ΔC_p [J/(g K)]	0.20	0.20	0.21	0.26	0.26	0.23	0.21
$T_{dec}{}^e$ [°C]	453	422	434	431	435	465	455

[a] As weighed molar amounts. [b] Determined from quantitative UV/vis spectroscopy. [c] Obtained from size exclusion chromatography with polystyrene standards and THF as eluent. [d] Glass transition temperature obtained from DSC (heating and cooling rate: 10 K/min). [e] Temperature for onset of weight loss in TGA (under nitrogen atmosphere).

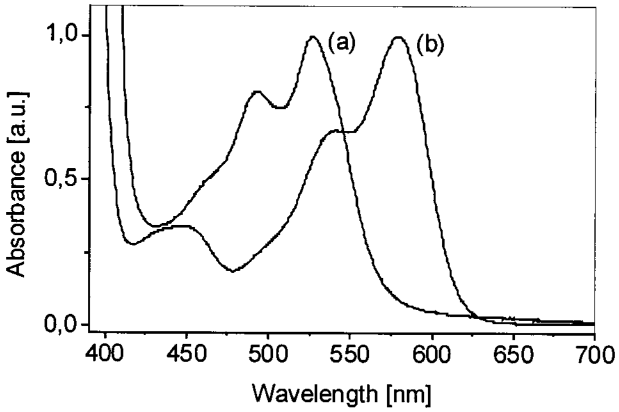


Figure 4. Normalized UV/vis spectra of (a) poly(quinoxaline perylene bisimide ether) (**8b**) and (b) poly(quinoxaline perylene bisimide) (**4e**) measured in $CHCl_3$ solution (absorption of polymer **8a** is similar to that of **8b**, and polymers **4b**–**d** resemble **4e**).

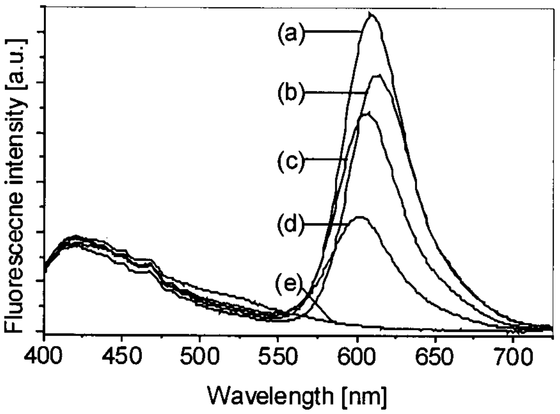


Figure 5. Dependence of fluorescence intensity and maximum wavelength of fluorescence emission (λ_{FL}) on perylene content for copolymers (a) **4d**, 1.0 mol %; (b) **4e**, 2.65 mol %; (c) **4c**, 0.5 mol %; (d) **4b**, 0.25 mol %; and (e) **4a** without perylene measured in films (thickness ~40 nm, excitation wavelength 370 nm).

polymers are given in Table 1. To confirm that all the perylene chromophore is covalently incorporated into the polymer main chain, the eluted sample in GPC was detected using both a refractive index detector (sensitive to the total polymer concentration in solution) and a wavelength-selective UV/vis absorption detector (at 563 nm for **4a**–**e** and 529 nm for **8a,b** corresponding to the characteristic maximum wavelength of absorption for perylene chromophore in both polymers). The chromatograms obtained using these two different detectors are very similar with single peaks at identical elution volumes, proving that the perylene dye is in fact incorporated into the polymer main chain and that no residual nonbound perylene chromophore is present in the polymer samples.

As expected, these polyimides and poly(imide ether)s are highly thermally stable, showing thermal decomposition onset only above 420 °C in thermogravimetric analysis (TGA) carried under a nitrogen atmosphere. Both types of polymers exhibit high glass transition temperatures (T_g), **4a**–**e** showing T_g values around 270 °C whereas **8a,b** having T_g values about 225 °C, indicating the influence of the flexibility of the ether linkage in the latter. Thus, these polymers fulfill the requirements of high-temperature stability and high T_g values as required for many electrooptical thin layer devices.

Figure 4 shows the UV/vis absorption spectra of **4e** and **8b** in $CHCl_3$ solution as examples for the two types of polymers. Within each copolymer series there is no shift in absorption maximum, indicating the absence of chromophore aggregation for these polymers with perylene content up to 2.82 mol % in the imide series and up to 0.43 mol % in the ether series. The vibronic structure of the absorption bands corresponds to the characteristic perylene π–π* electronic transition. In general, the maximum wavelength of absorption λ_{Abs} of perylene diimides depends on the substitution pattern of the perylene core as well as on the interaction of the chromophore units.[2,23,24] The polymers **4b**–**e** with tetraphenoxy-substituted perylene core show λ_{Abs} at 578 nm whereas the poly(imide ether)s **8a,b** with only two "phenoxy substituents" at bay positions absorb at shorter wavelength with $\lambda_{Abs} = 527$ nm. This observed bathochromic shift of λ_{Abs} with higher degree of phenoxy substitution arises from the increased electron-donating nature of phenoxy substituents. This behavior is observed in low molecular weight perylene imides also. This fact enables us to tune the absorption as well as fluorescence emission in such polymers.

Polymers **4b**–**e** and **8a,b** show intense reddish-orange fluorescence in dilute solutions and in thin films. The intensity of fluorescence emission in solution and in the solid state as well as its dependence on the amount of incorporated perylene was studied by measuring fluorescence of the copolymers in dilute chloroform solutions and in thin films (thickness ~ 100 nm). The variation in fluorescence intensity of the polymers **4a**–**e** in thin films is depicted in Figure 5. The intensity of maximum wavelength of emission λ_{FL} increases with increase in amount of perylene in the polymer up to an amount of 1.15 mol % (polymer **4d**). Further increase in perylene content decreases the emission intensity. Thus, maximum solid-state fluorescence is obtained for the polymer **4d**, in which case the concentration-dependent fluorescence quenching is at a minimum. The λ_{FL} values for the polymers **4b**–**e** are between 605 and 614 nm.

Polymers **8a,b** exhibit λ_{FL} values of 552 and 557 nm, respectively. On comparing the wavelength of fluorescence emission of the poly(imide ether)s **8a,b** with those of **4b**−**e**, a bathochromic shift in λ_{FL} (similar to λ_{Abs}) of about 60 nm is observed for the latter. These results obviously indicate that a tuning of the color of emission and an optimization of perylene content for obtaining maximum fluorescence intensity in thin films of perylene imide polymers were achieved using our synthetic strategy of copolymerization.

It can be concluded that all these highly fluorescent polymers are potential candidates for charge generation by absorption of light followed by charge separation and transfer, thus making them attractive for fluorescence studies, electron-transfer phenomena in solar cells, etc. An effective method to study the electron transfer between two molecules resulting from photoexcitation is to examine the photoluminescence quenching observed on blending such electron transport perylene polymers with hole transport molecules. In this context, we examined the fluorescence properties of some of these polymers after blending with varying amounts of conventional hole-conducting molecules like triphenyldiamines as well as polymeric triphenyldiamines. A complete quenching of perylene fluorescence is observed for blends with polymeric triphenyldiamine content of 17%, 25%, and 50% (w/w). Further investigations regarding the applicability of these polymers in thin-layer solar cells is the subject matter of our current research activity. The high fluorescence emission properties of these copolymers can also be exploited for the realization of organic light-emitting diodes by using them as electron transport and emission materials.

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