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An Efficient Synthesis of Quaterrylenedicarboximide NIR Dyes

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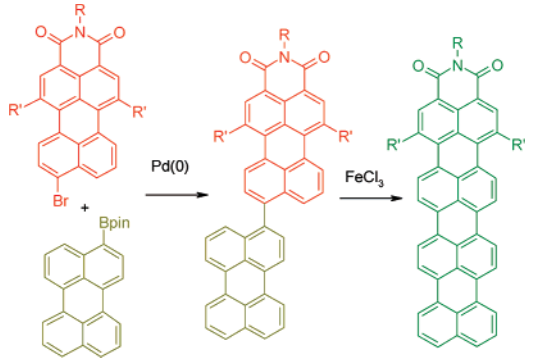
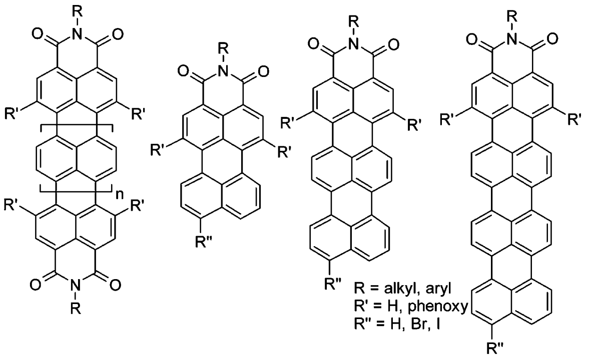


Quaterrylenedicarboximides were prepared from 9-bromoperylene-3,4-dicarboximides by palladium-catalyzed coupling with 3-perylene boronic ester, followed by oxidative cyclodehydrogenation of the resulting perylene−perylenedicarboximide dyads with iron(III) chloride. The quaterrylenedicarboximides, described here, are highly photochemically and thermally stable dyes, which may be useful as green NIR dyes (λ_{max} = 735 nm) and as building blocks for the synthesis of higher rylene dyes.

Rylenebis(dicarboximide)s, **1** (Figure 1), are photochemically and thermally stable dyes which absorb in the visible (n = 0, 1) and the near-infrared ranges (n = 2−4). Whereas perylenebis(dicarboximide)s (n = 0, λ_{max} = 524 nm) with a variety of applications[1] are well-described, the syntheses of terrylene- (n = 1, λ_{max} = 660 nm)[2] and quaterrylenebis(dicarboximide)s[3,4] (n = 2, λ_{max} = 760 nm) have been reported only in the past decade. The syntheses of **1a**−**c** have been achieved by direct base-induced homo-[4] or heterocoupling[2,3] of naphthalene- and perylenedicarboximides **2**, which contain only one imide group in the molecule as compared to rylenebis(dicarboximides) **1**. The synthesis of higher homologues required initial coupling of perylene- and terrylenedicarboximides with a single bond and then base-induced cyclodehydrogenation of the precursors into penta- and hexarylenebis(dicarboximides) **1d**−**e**.[5] This two-step approach required compounds **2** and **3** as synthetic building blocks. Perylenedicarboximides **2** (PMIs, λ_{max} = 520 nm), which are easily available by the imidization−decarboxylation route,[6] are useful as highly fluorescent orange dyes[7] and precursors for the synthesis of other dyes.[2,3,5,8] A multistep route to terrylenedicarboximide **3** (λ_{max} = 643 nm) was recently described and used for the synthesis of higher rylenes only.[5] Although the formation of a quaterrylenedicarboximide−perylenedicarboximide dyad was previously reported during the synthesis of **1e**,[5] the isolation and characterization of the higher homologue of **2** and **3**, quaterrylenedicarboximide **4** (QMI), until now has not been described. The synthesis of **4** as a dye, which is expected to have an intense absorption in the NIR region and be useful as a synthetic building block for the synthesis of higher rylene dyes (due to the free *peri*-positions) seems to be an important target in modern dyestuff chemistry.



1a-e n = 0-4 **2** **3** **4**

FIGURE 1. Rylenebis(dicarboximides) **1** and rylenedicarboximides **2**−**4**.

In this Note, we present a facile synthetic route to QMIs having the general formula **4** and an absorption maxima at 735−740 nm starting from PMI and perylene. The key units in our synthetic approach (Scheme 1) are perylene derivatives **2** and **6**, which are functionalized on one side only. The preparation of PMI derivatives **2** was achieved by known procedures.[5,9] 3-Bromoperylene was obtained in 92% yield by NBS bromi-

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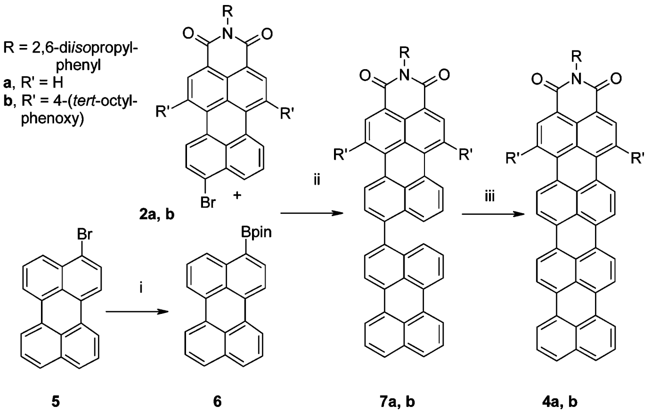
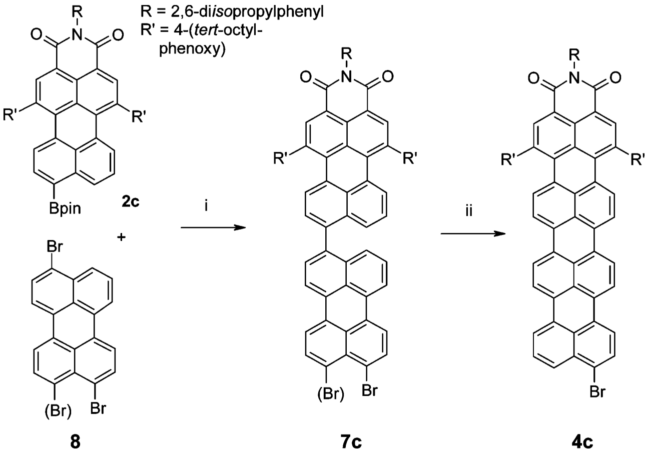
SCHEME 1[a]



[a] Conditions: (i) $B_2(pin)_2$, dioxane, KOAc, 70 °C, 15 h, 91%; (ii) $Pd(PPh_3)_4$, aq K_2CO_3, toluene, 95 °C, 15 h, 72% (a), 81% (b); (iii) $FeCl_3$/$MeNO_2$, CH_2Cl_2, 25 °C, 24 h, 80% (a), 54% (b).

SCHEME 2[a]



[a] Conditions: (i) $Pd(PPh_3)_4$, aq K_2CO_3, toluene, 70 °C, 6 h, 69%; (ii) $FeCl_3$/$MeNO_2$, CH_2Cl_2, 25 °C, 24 h, 60%.

nation of perylene in DMF.[10,11] For the synthesis of perylene−PMI dyads, active boronic esters of PMI were initially considered.[5,9] However, the chromatographic purification of these esters on silica gel was plagued by the sticking of the product on the column, and low yields were consequently obtained. However, conversion of 3-bromoperylene **5** into the previously unknown boronic ester **6** circumvented this problem, and the product could be isolated in 91% yield.

The preparation of perylene−PMI dyads **7a**,**b** was achieved by palladium-catalyzed Suzuki cross-coupling of 9-bromoPMI derivatives **2a**,**b** with perylene boronic ester **6**. After the chromatographic purification, the dyads **7a**,**b** were isolated as dark red solids in high yields (60−80%). The next step was the oxidative cyclodehydrogenation of dyads **7a**,**b** into the target QMI molecules **4a**,**b**. The known method for conversion of bisPMI precursors into **1c** uses base-assisted cyclodehydrogenation (molten KOH/glucose, K_2CO_3/ethanolamine, *t*-BuOK/DBN), which requires the presence of strong electron-withdrawing groups on both parts of the precursor.[2,3,5] However, dyads **7a**,**b** only contain such groups in the PMI component. Therefore, other conditions for the cyclodehydrogenation had to be used.

Cationic cyclodehydrogenation of **7** with aluminum chloride, which had previously been applied successfully for terrylene synthesis,[12] afforded a green product in which the desired bond had been formed. However, MALDI-TOF mass spectrometry revealed that it was a mixture of QMIs containing significant amounts of chlorinated and dealkylated derivatives. Therefore, milder conditions for the cyclodehydrogenation had to be employed to avoid side reactions. Iron(III) chloride is known as a mild oxidizing agent for the cyclodehydrogenation of hexaphenylbenzenes to hexabenzocoronenes.[13] Recently, this reagent was successfully applied for the preparation of novel perylene chromophores from substituted acenaphthenes[14] and for the fusion of poly(perylene) to poly(quaterrylene).[15] Cyclodehydrogenation of **7** with an 8−10-fold excess of $FeCl_3$ led to the formation of the desired QMI chromophores **4a**,**b** in good yields (55−80%).

The synthesis of monobromoQMI required another approach (Scheme 2). Since the selective bromination of **4a**,**b** is a challenge, the active boronic ester of PMI **2c** was allowed to react with an excess of 3,9(10)-dibromoperylene[11] **8** under mild conditions to give dyad **7c**. Both the starting dibromoperylene **8** and dyad **7c** consist of a mixture of two regioisomers that are not separable by column chromatography. This is no consequence because cyclodehydrogenation of each isomer affords the same product, namely, 13-bromoQMI **4c**. Fortunately, this reaction was not accompanied by halogen exchange. The regioselective synthesis of monofunctional dye **4c**, which contains a bromide in a free *peri*-position, not only provides an opportunity to use this dye as NIR label but also to tune the electronic properties via the introduction of donor or acceptor groups or to generate even larger chromophoric systems.

QMIs **4a**−**c** possess different solubilities depending on their substituents. Compound **4a** is only slightly soluble in organic solvents at room temperature and is better regarded as a pigment than a dye. The introduction of bulky *tert*-octylphenoxy groups into the bay region of starting PMI **2b** enhanced the solubility of **4b** as compared to **4a**. However, the presence of the planar, highly hydrophobic part of the molecule leads to aggregation in solution. This was confirmed by NMR spectroscopy since the signals of quaterrylene protons appeared as broad peaks at room and even at higher temperatures (up to 400 K). Only by using a dilute solution (1 mg/mL) in 1,3,5-trichlorobenzene-d_3 at 443 K allowed for the observation of narrow resonance signals. A full assignment of the signals was achieved using a $^1H-^1H$ COSY experiment.

The absorption spectrum of dyad **7b** (Figure 2) consists of distinct perylene and PMI parts, which are bathochromically shifted compared to their parent chromophores due to π-conjugation. When the dyad was excited at 418 nm (perylene absorption only), PMI emission ($\lambda_{max} = 604$ nm) was observed.

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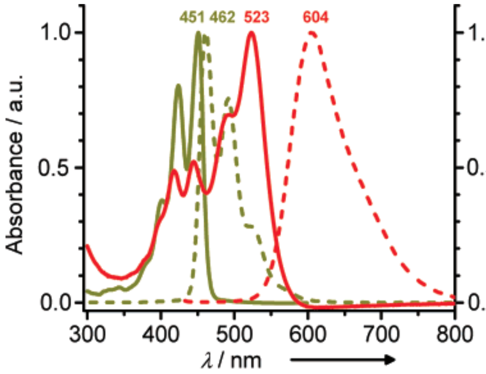

FIGURE 2. Normalized spectra of perylene **6** (yellow), solid line = absorption, dashed line = emission (λ_{exc} = 450 nm); PMI−perylene dyad **7b** (red), solid line = absorption, dashed line = emission (λ_{exc} = 418 nm). Solvent = toluene.

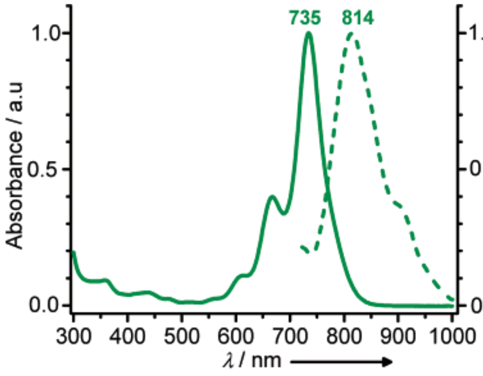

FIGURE 3. Normalized spectra of QMI **4b** in toluene, solid line = absorption, dashed line = emission (λ_{exc} = 680 nm).

The absence of the perylene component in the emission of dyad **7** can be attributed to the substantial overlap between the emission spectrum of the perylene part of the molecule and the absorption spectrum of the PMI part, which allows for efficient energy transfer. DiphenoxyQMI **4b** shows a bright green color in solution with an absorption maximum at 735 nm (Figure 3). As compared to parent PMI **2** (λ_{max} = 520 nm), the absorption is shifted bathochromically by 215 nm, owing to the greater size of the chromophore. A significant increase of the molar absorption coefficient from 37 000 (for **2b**)[5] to 143 000 (for **4b**) is also observed. The spectrum is similar to that of QDI **1c**, but the bands are shifted hypsochromically by 45 nm as compared to tetraphenoxy dye (R′ = phenoxy). Similar to QDI **1c**,[3] the dye **4b** shows only a very weak emission (ϕ_F = 0.15%). The emission spectrum (Figure 3) reveals mirror symmetry with the absorption spectrum and a large Stokes shift (80 nm). This finding, together with a broadening of the emission bands, additionally supports high aggregation of QMI molecules in solution. To avoid the complications associated with aggregation, the emission of QMI derivatives should ideally be tested by single molecule spectroscopy.[16]

The photostability of the QMI **4b** was estimated by exposing a nondegassed solution to UV light for a prolonged period of time. The absorbance dropped to 87% of its initial value after 18 h of irradiation. Thus, the QMI chromophore shows slightly lower photostability than perylenebis(dicarboximide)s **1a**, which are known for their excellent photostabilities.[17] The presence of free active *peri*-positions in QMI dyes, which can be susceptible to photooxidation, may explain this decrease of the photostability. According to thermogravimetric analysis, compound **4b** is thermally stable up to 380 °C. Such a high thermal stability is important for its practical applications, such as blending with thermoplastics during processing.

The synthesis and spectroscopic data for new NIR chromophores, quaterrylenedicarboximides, are described. Depending on its structure, the new chromophore **4** may be a pigment (**4a**) or a soluble dye (**4b**) that is expected to have a wide range of applications. These dyes display narrow absorption peaks in the range of 730−740 nm and weak fluorescence in solutions with an emission at 814 nm. The incorporation of a bromide into the free *peri*-position offers the possibility of using the dye **4c** as NIR labels, as in spectroscopic optical coherence tomography, where a sharp absorption at 740 nm is required.[18] Moreover, one can envision the potential application of **4c** as a synthetic precursor for the synthesis of new core-extended rylene dyes, like **1** (*n* = 5, 6).

Experimental Section

General: The solvents and chemicals used were of commercial grade. Compounds **2a**−**c** were synthesized as described elsewhere.[5,9] Column chromatography was performed on silica gel (Silicagel 60A, 0.06−0.2 mm, Acros). Melting points were performed on a Büchi MP B-545 melting point apparatus and are not corrected. Thermal gravimetric analyses were performed using Mettler TGA851e apparatus. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX250, Bruker AMX300, Bruker DRX500, and Bruker WS700 spectrometers. Infrared spectra were obtained on a Nicolet FTIR320. FD mass spectra were recorded with a VG Instruments ZAB 2-SE-FPD instrument. MALDI-TOF mass spectra were recorded on a Bruker Reflex II-TOF spectrometer. UV/vis spectra were recorded on a Perkin-Elmer Lambda 900 spectrophotometer. Fluorescence spectra were recorded on a Spex Fluorolog 3 spectrometer. Fluorescence quantum yield of compound **4b** was determined by the relative method using Rhodamine 800 as a reference (ϕ_F = 39% in dichloroethane[19]). Elemental analyses were performed on a Foss Heraeus Vario EL in the Institute for Organic Chemistry at the University of Mainz.

3-(4,4,5,5-Tetramethyl-1,3-dioxa-2-borolan-2-yl)perylene (6). A mixture of 3-bromoperylene (0.99 g, 3 mmol), bis(pinacolato)-diboron (1.14 g, 4.5 mmol), Pd(dppf)$_2$Cl$_2$ (90 mg, 0.1 mmol), and 1,4-dioxane (150 mL) was flushed with argon for 20 min in a 250 mL Schlenk flask. Potassium acetate (0.9 g, 9 mmol) was added, and then the mixture was stirred under argon at 70 °C for 15 h. The mixture was evaporated to dryness, dissolved in a minimal volume of dichloromethane, and placed on the top of a sinter funnel loaded with dry silica gel (10 × 10 cm). The funnel was eluted with petroleum ether/dichloromethane (1:1) under vacuum. The first colored fractions were combined and evaporated. The product (1.12 g) contains less than 10% of impurities (MS data) and was used in next reactions without additional purification. For analytical purposes, the sample of the product (100 mg) was purified by the column chromatography (silica gel, petroleum ether/dichloromethane (1:1)): yield 92 mg (91%); mp 233 °C; R_f = 0.26 (hexane/dichloromethane, 3:1); ^{1}H NMR (250 MHz, CD$_2$Cl$_2$,

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25 °C) δ 8.65 (d, $^3J = 8.4$ Hz, 1H), 8.26 (d, $^3J = 7.3$ Hz, 2H), 8.20 (d, $^3J = 7.4$ Hz, 2H), 8.04 (d, $^3J = 7.6$ Hz, 1H), 7.72 (t, $^3J = 7.6$ Hz, 2H), 7.48−7.57 (m, 3H), 1.43 (s, 12H) ppm; ^{13}C NMR (75 MHz, $C_2D_2Cl_4$, 25 °C) δ 138.2, 136.0, 134.3, 133.8, 131.2, 131.0, 130.9, 130.8, 128.5, 128.4, 127.9, 127.7, 126.8, 126.7, 126.6, 120.9, 120.4, 120.2, 120.1, 119.3, 83.7, 24.9 ppm; IR (KBr) ν 3420, 2970, 2920, 1499, 1369, 1350, 1324, 1272, 1144, 1120, 849, 813, 772 cm^{-1}; UV−vis (toluene) λ_{max} (ϵ) 451 (31100), 424 (24900), 401 (11700) nm; fluorescence (toluene) λ_{max} 462, 491 nm; MS (FD) *m*/*z* (rel. int.) 378.59 (100%), M$^+$. Anal. Calcd for $C_{26}H_{23}BO_2$: C, 82.55; H, 6.13. Found: C, 82.62; H, 6.07.

***N*-(2,6-Diisopropylphenyl)-1,6-bis(4-(1,1,3,3-tetramethylbutyl)phenoxy)-9-(perylen-3-yl)perylene-3,4-dicarboximide (7b).** *N*-(2,6-Diisopropylphenyl)-1,6-bis(4-(1,1,3,3-tetramethylbutyl)phenoxy)-9-bromoperylene-3,4-dicarboximide (194 mg, 0.2 mmol) and compound **6** (115 mg, 0.3 mmol) were dissolved in the mixture of toluene (40 mL) and ethanol (2 mL) in a 100 mL Schlenk flask and flushed with argon. After stirring at 95 °C for 20 min, 2 M aqueous K_2CO_3 (0.5 mL) and $Pd(PPh_3)_4$ (20 mg, 0,02 mmol) were added to the solution. The reaction mixture was stirred at 100 °C for 20 h under argon. After cooling, the resulting mixture was washed with water and extracted with toluene. The combined organic extracts were evaporated in vacuo and purified by column chromatography on silica gel using toluene as an eluent: yield 185 mg (81%); mp 300 °C; $R_f = 0.66$ (toluene); ^{1}H NMR (250 MHz, CD_2Cl_2, 25 °C) δ 9.50 (d, $^3J = 8.0$ Hz, 1H), 9.38 (d, $^3J = 7.8$ Hz, 1H), 8.36 (d, $^3J = 7.9$ Hz, 1H), 8.31 (d, $^3J = 7.6$ Hz, 1H), 8.25−8.28 (m, 3H), 7.76 (d, $^3J = 7.9$ Hz, 2H), 7.66 (t, $^3J = 9.1$ Hz, 2H), 7.42−7.59 (m, 10H), 7.32 (dd, $^3J = 7.7$ Hz, $^4J = 3.7$ Hz, 4H), 7.14 (d, $^3J = 8.7$ Hz, 2H), 7.09 (d, $^3J = 8.8$ Hz, 2H), 2.72 (sep, $^3J = 6.8$ Hz, 2H), 1.75 (s, 2H), 1.74 (s, 2H), 1.39 (s, 6H), 1.38 (s, 6H), 1.11 (d, $^3J = 6.7$ Hz, 12H), 0.73 (s, 9H), 0.72 (s, 9H) ppm; ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 25 °C) δ 163.0, 153.7, 153.0, 146.4, 145.4, 140.5, 137.5, 134.5, 129.1, 128.4, 127.4, 126.4, 123.9, 121.2, 121.2, 120.5, 120.4, 119.9, 118.3, 57.0, 53.7, 38.1, 31.6, 31.3, 29.6, 28.9, 23.9 ppm; IR (KBr) ν 3440, 2956, 2924, 2853, 1705, 1669, 1596, 1503, 1465, 1332, 1261, 1209, 1125, 1094, 810 cm^{-1}; UV−vis (toluene) λ_{max} (ϵ) 523 (64700), 492 (45000), 446 (33500), 418 (31600) nm; fluorescence (toluene) λ_{max} 604 nm; MS (FD) *m*/*z* (rel. int.) 1140.6 (100%), M$^+$. Anal. Calcd for $C_{82}H_{77}NO_4$: C, 86.36; H, 6.81; N, 1.23. Found: C, 86.46; H, 6.74; N, 1.18.

***N*-(2,6-Diisopropylphenyl)-1,6-bis(4-(1,1,3,3-tetramethylbutyl)phenoxy)quaterrylene-3,4-dicarboximide (4b).** Compound **7b** (200 mg, 0.175 mmol) was dissolved in dry dichloromethane (10 mL) in a 25 mL Schlenk flask. After stirring for 20 min under argon, a solution of anhydrous iron(III) chloride (285 mg, 1.75 mmol) in dry nitromethane (2 mL) was added through a syringe. The solution was stirred at room temperature for 24 h. Dry methanol (50 mL) was added to the solution. The resulting precipitate was filtered, rinsed with methanol, and dried. The precipitate was purified by the column chromatography on silica gel using toluene as eluent: yield 108 mg (54%); mp >350 °C; $R_f = 0.52$ (toluene); ^{1}H NMR (700 MHz, 1,3,5-trichlorobenzene-d_3, 170 °C) δ 9.65 (d, $^3J = 8.6$ Hz, 2H), 8.58 (s, 2H), 8.44 (d, $^3J = 8.8$ Hz, 2H), 8.39 (d, $^3J = 8.2$ Hz, 2H), 8.34 (d, $^3J = 8.3$ Hz, 2H), 8.28 (d, $^3J = 7.6$ Hz, 2H), 7.73 (d, $^3J = 7.9$ Hz, 2H), 7.54 (d, $^3J = 7.8$ Hz, 2H), 7.52 (d, $^3J = 8.8$ Hz, 4H), 7.41 (t, $^3J = 7.6$ Hz, 1H), 7.31 (d, $^3J = 7.9$ Hz, 2H), 7.29 (d, $^3J = 8.4$ Hz, 4H), 3.00 (sep, $^3J = 6.8$ Hz, 2H), 1.88 (s, 4H), 1.51 (s, 12H), 1.28 (d, $^3J = 6.8$ Hz, 12H), 0.92 (s, 18H) ppm; ^{1}H−^{1}H COSY experiment (700 MHz, 1,3,5-trichlorobenzene-d_3, 170 °C) coupling of δ = (9.65, 8.44), (8.39, 8.34), (8.28, 7.54), (7.73, 7.54), (7.52, 7.29), (7.41, 7.31); IR (KBr) ν 3449, 2956, 2923, 2853, 1700, 1664, 1585, 1502, 1466, 1320, 1302, 1272, 1203, 1172, 806 cm^{-1}; UV−vis (toluene) λ_{max} (ϵ) 734 (143000), 668 (57000), 614 (15700), 358 (13300) nm; fluorescence (toluene) λ_{max} 814 nm; MS (FD) *m*/*z* (rel. int.) 1138.6 (100%), M$^+$. Anal. Calcd for $C_{82}H_{75}NO_4$: C, 86.51; H, 6.64; N, 1.23. Found: C, 86.58; H, 6.61; N, 1.19.

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Supporting Information Available: Experimental procedures, characterization for compounds **4a**, **4c**, **7a**, and **7c** and ^{1}H and ^{13}C NMR spectra for **4a**−**c**, **6**, and **7a**−**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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