DOI: 10.1002/ejoc.200800211

Fluorescent Bis(oligophenylylamino)terephthalates

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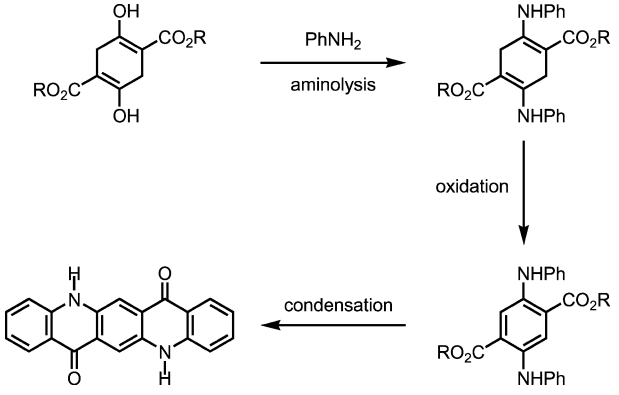
Keywords: Enamines / Cross coupling / Fluorescence / Oligophenylenes / Oxidation / Terephthalates

The reaction of succinyl succinates with aniline, iodoaniline and iodobiphenylamine yielded 2,5-bis(arylamino)-terephthalates. Suzuki cross-coupling reactions of the iodo-functionalized compounds with phenyl- and biphenylyl-boronic acids gave 2,5-diaminoterephthalates with *N*-biphenylyl, *N*-terphenylyl and *N*-quaterphenylyl substituents. Some of the products show interesting fluorescence behaviour.

Introduction

Since the first report by Liebermann in 1914,[1] the reaction of succinyl succinates with aniline has developed into an extraordinarily important step in the synthesis of 2,5-diaminoterephthalates. These compounds are essential precursors for the industrial synthesis of quinacridone pigments, which involves three steps: aminolysis (enamine formation), oxidative aromatization and condensation (Scheme 1).[2]



Scheme 1. Industrial synthesis of quinacridone pigments from succinyl succinates.

In close relation to our recent work on double-Michael reactions with succinyl succinates[3] we were interested in improving the solubility of *p*-functionalized *p*-terphenylyl- and *p*-quaterphenylylamines by attaching them to terephthalate moieties. Oligo-*p*-phenylenes have proven to be versatile building blocks for the generation of self-assembled nanoaggregates with interesting optical properties.[4] A major drawback of these materials, however, is their very low solubility, which makes their purification and handling relatively difficult. In order to improve this property, we planned to build up *p*-phenylene units by Suzuki cross-coupling reactions on a terephthalate scaffold with octyl ester groups.

Results and Discussion

The reaction of succinyl succinates **1** with aniline derivatives **2** to give 2,5-diaminoterephthalates **3a**–**3f** proceeds via a mono- and a bis-enamine and is completed by oxidative aromatization. The latter step has been reported to be achieved with stoichiometric amounts of bromine.[5] In our hands this oxidation step proceeded quickly in the presence of catalytic amounts of Pd on charcoal with atmospheric oxygen.[6] However, as the mono-enamine can also oxidize to give the aminohydroxyterephthalic acid derivative, careful control of reaction conditions, in particular, the partial pressure of oxygen, was crucial for the success of this reaction. Finally, it turned out that oxidative aminolysis is best performed without any Pd or other catalyst by simple heating of the starting materials in air (Scheme 2, Table 1).[7] Reactions of the ethyl and octyl esters **1a** and **1b** with aniline (**2a**) and iodoaniline (**2b**) proceeded with good yields (86–93%) at 60 °C in toluene in the presence of catalytic amounts of HCl. The better solubility of the octyl esters **3b** and **3d** facilitated purification by column chromatography or recrystallization. The reactions of **1a** and **1b** with biphenyl derivative **2c** was performed in AcOH at 100 °C and the yields of the products **3e** and **3f** were satisfactory (both 67%). The preparation of starting materials **1a** and **1b** has been reported previously.[3] The iodobiphenylamine (**2c**) was prepared in two steps from biphenyl (**4**) by following two literature procedures (Scheme 3).[8] The first step is an

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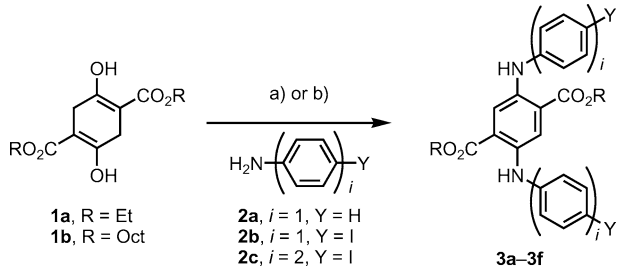
Table 1. Synthesis of diaminoterephthalates **3a**–**3f** and their spectroscopic properties.[a]

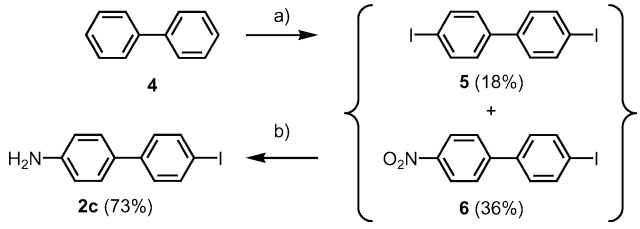
Product	Starting materials	R	*i*	Y	% Yield	λ_{max}[b] [nm]	ε [dm^3 mol^{-1} cm^{-1}]	λ_{em} [nm]	Φ
3a	**1a**, **2a**	Et	1	H	89	326	29200	577	0.096
3b	**1b**, **2a**	Oct	1	H	92	325	28500	589	0.23
3c	**1a**, **2b**	Et	1	I	86	337	23200	573	0.10
3d	**1b**, **2b**	Oct	1	I	93	337	34000	570	0.10
3e	**1a**, **2c**	Et	2	I	67	355	53500	–	–
3f	**1b**, **2c**	Oct	2	I	67	356	43000	586	0.075

[a] The spectroscopic data were determined for solutions in CH_2Cl_2. [b] Only the largest of three absorption bands is listed.

electrophilic nitration/iodination that yields an inseparable mixture of 4,4′-diiodobiphenyl (**5**) and 4-iodo-4′-nitrobiphenyl (**6**). After reduction of this mixture the amino compound **2c** can be separated from the diiodo compound **5**.

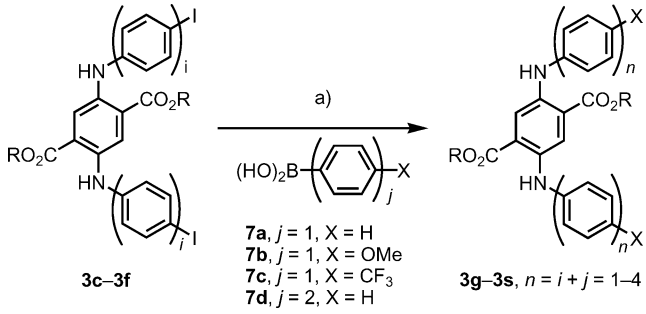


Scheme 2. Synthesis of fluorescence materials **3a**–**3f** by oxidative aminolysis of succinyl succinates **1**. For yields and substituents R and Y, see Table 1. Reagents and conditions: a) cat. HCl, air, toluene, 60 °C, 2 d (for **3a**, **3b**, **3d**), 16 h (for **3c**); b) air, AcOH, 100 °C, 16 h (for **3e**, **3f**).



Scheme 3. Two-step synthesis of biphenyl derivative **2c**. Reagents and conditions: a) 1 equiv. I_2, 2.5 equiv. concd. HNO_3, 5 equiv. concd. H_2SO_4, AcOH, 110 °C, 2 h; b) Zn, HCl, EtOH, 78 °C, 1 h.

The Suzuki cross-coupling reaction of iodo compounds **3c**–**3f** with boronic acids **7a**–**7d** was performed according to a standard protocol.[9] [$Pd(PPh_3)_4$] (5 mol-%) was used as the catalyst, Na_2CO_3 as the base. The reactions proceeded in toluene/EtOH/water at reflux overnight. After work up, the products **3g**–**3s** directly crystallized from the organic extracts. Again, the yields of the octyl esters are (with two exceptions) better than those of the ethyl esters as purification of the latter is difficult due to lower solubility. All the compounds **3g**–**3s** were obtained as deeply coloured (red to violet in solution) crystalline materials in 42–85% yield (Scheme 4, Table 2). Even in highly dilute solutions, they show fluorescence behaviour. For terephthalates with biphenyl (n = 2) and terphenyl (n = 3) moieties, electron-do-



Scheme 4. Synthesis of fluorescence materials **3g**–**3s** by Suzuki cross-coupling reaction. For yields and substituents R and X, see Table 2. Reagents and conditions: a) 5 mol-% [$Pd(PPh_3)_4$], 4 equiv. Na_2CO_3, toluene/EtOH/H_2O (1:1:1.5), reflux, 16 h.

Table 2. Preparation of the fluorescent materials **3g**–**3s** by Suzuki cross-coupling and their spectroscopic properties.[a]

Product	Starting materials	R	$n = i + j$	X	% Yield	λ_{max} [nm]	ε [dm^3 mol^{-1} cm^{-1}]	λ_{em} [nm]	Φ
3g	**3c**, **7a**	Et	2	H	70	350	43200	592	0.036
3h	**3d**, **7a**	Oct	2	H	49	350	44600	589	0.052
3i	**3c**, **7b**	Et	2	OMe	42	348	37900	602	0.013
3j	**3d**, **7b**	Oct	2	OMe	42	348	47000	603	0.028
3k	**3c**, **7c**	Et	2	CF_3	55	359	37700	581	0.074
3l	**3d**, **7c**	Oct	2	CF_3	57	359	38000	581	0.11
3m	**3c**, **7d**	Et	3	H	54	355	38400	–	–
3n	**3d**, **7d**	Oct	3	H	72	359	48300	592	0.046
3o	**3e**, **7b**	Et	3	OMe	60	358	33900	–	–
3p	**3f**, **7b**	Oct	3	OMe	85	359	60800	593	0.028
3q	**3e**, **7c**	Et	3	CF_3	61	365	13500	–	–
3r	**3f**, **7c**	Oct	3	CF_3	73	287,[b] 362	38400,[b] 30700	589	0.069
3s	**3f**, **7d**	Oct	4	H	42	305,[b] 355	39800,[b] 23700	–	–

[a] For details, see Table 1. [b] The first of the three bands, showing the largest intensity.

nating (X = OMe) and -withdrawing (X = CF_3) substituents were introduced, originating from the corresponding boronic acids **7b** or **7c**.

In order to gain an insight into the structural features of the compounds, crystal structure determinations of **3b** and **3d** were performed at T = 100 K with $R(F)$ = 0.0821 and 0.0243, respectively.[10] The former compound (**3b**) crystallizes in the monoclinic $P2_1/c$ space group and has the parameters a = 7.776(3), b = 37.825(15), c = 11.053(4) Å, β = 92.29(3)°. There are two independent molecules in the unit cell, each having crystallographic $\bar{1}$ (C_s) symmetry and a similar geometry, therefore only one (labelled as a) is shown in Figure 1. The C–N distances [N(a)–C8a 1.389(4) and N(a)–C6a 1.411(4) Å], shorter than for the typical single C–N bond (1.47 Å), and the C8a–N(a)–C6a angle [127.1(3)°] indicate that the C–N bonds have partial π character. The planes of the peripheral phenyl rings are, however, twisted 51.0° with respect to the central benzene ring.

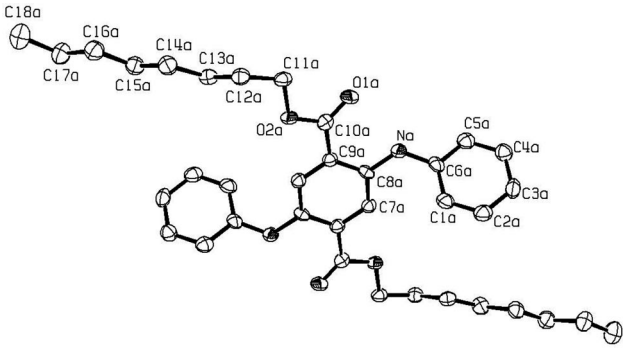


Figure 1. ORTEP view of one (molecule a) of the two independent molecules of compound **3b** in the unit cell.

Compound **3d** (Figure 2) forms triclinic crystals with the space group $P\bar{1}$ and has the parameters a = 4.500(3), b = 11.144(8), c = 17.238(12) Å, α = 88.56(6), β = 88.63(5), γ = 89.05(5)°. As in the previous example the molecules are crystallographically centrosymmetric. The parameters of the C4–N–C8 fragment are also similar [C4–N 1.400(3) Å, C8–N 1.400(3) Å and C4–N–N8 127.5(2)°]. The twisting of the peripheral phenyl rings (–41.8°) with respect to the central benzene ring is, however, less than in the previous case. Note that the presence of long octyl chains results in bending of the carboxy group towards the phenyl rings in the two molecules, which is reflected in the values of the C–C–O angles: O2a–C10a–C9a 112.9(3) (**3b**, molecule a), O2b–C10b–C9b 113.5(3) (**3b**, molecule b) and O2–C10–C9 112.4(2)° (**3d**). At the same time the O–C–C angles are O1a–C10a–C9a 125.4(3) (**3b**, molecule a), O1b–C10b–C9b 125.7(3) (**3b**, molecule b) and O1–C10–C9 125.1(2)° (**3d**).

The results of the preliminary spectroscopic investigations of compounds **3a**–**3d**, **3f**–**3l**, **3n**, **3p** and **3r** are collected in Tables 1 and 2. Generally they all show three bands in the absorption range 220–600 nm. The first band is located near 230–240 nm and has a large molar absorption coefficient (between 20000 and 40000 $dm^3 mol^{-1} cm^{-1}$). The second is with two exceptions the most intense (ε between 23200 and 60800 $dm^3 mol^{-1} cm^{-1}$) and lies between 325 and 370 nm. The third, the weakest one (ε between 6800 and 9500 $dm^3 mol^{-1} cm^{-1}$), occurs near 465 nm. In the cases of compounds **3r** and **3s**, the first band has the highest intensity and is therefore listed in Table 2 together with the second band. Compounds **3** are orange luminophores (the emission maxima were located between 570 and 603 nm). The absorption and emission spectra for **3d** are given as examples in Figure 3.

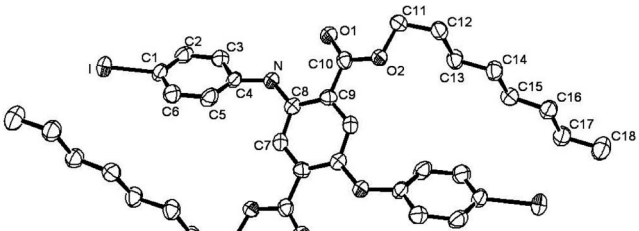


Figure 2. ORTEP representation of the structure of compound **3d** in the solid state.

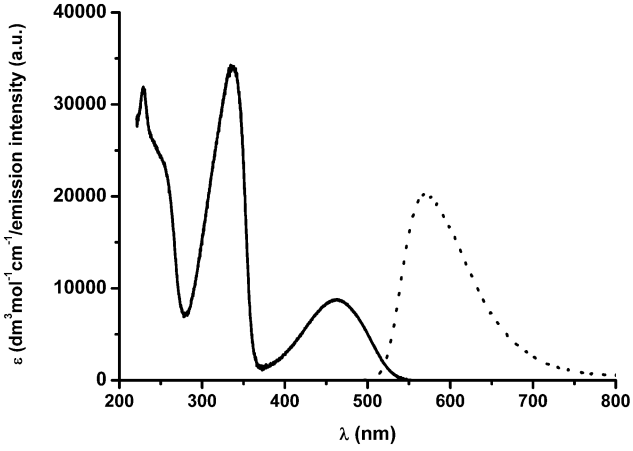


Figure 3. The absorption (solid) and emission (dotted) spectra of **3d**. The absorption spectrum is shown in molar absorption units; the emission spectrum (excited by 350 nm light) is given in arbitrary units.

The luminescence was excited with 350 or 320 nm radiation. However, when some of the samples (namely those with biphenyl or terphenyl moieties, **3g**, **3i**–**3k**, **3n**, **3p** and **3r**) were excited with 300 nm light, additional emission bands with maxima located below 400 nm were observed. For **3r**, this emission (with a maximum at 384 nm) even dominated the orange luminescence, the latter being faint in this case. Moreover, an additional emission band with a maximum at 784 nm appeared (Figure 4). Quantum yields were determined with an external standard (aqueous solution of $[bpy_3Ru]Cl_2$) and calculated using a modified Parker–Rees method.[11]

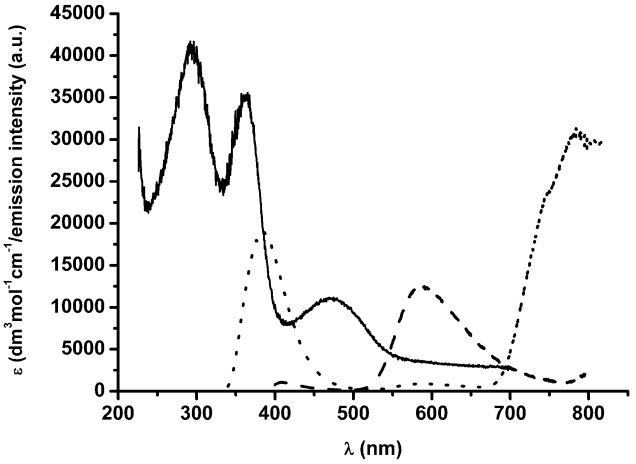


Figure 4. The absorption (solid) and emission [excited at 350 nm (dashed) and 300 nm (dotted)] spectra of **3r**. The absorption spectrum is shown in molar absorption units and the emission spectra in arbitrary units.

Conclusions

In summary, (oligophenylyl)amino-substituted terephthalates have been readily accessed in two steps: oxidative aminolysis of succinyl succinates with aniline derivatives followed by Suzuki cross-coupling. Diethyl and dioctyl esters **1a** and **1b** were utilized as electrophiles in the first step. As amines, aniline (**2a**), iodoaniline (**2b**) and iodobiphenylamine (**2c**) were used. Four different boronic acids were used in the cross-coupling step: $PhB(OH)_2$ (**7a**), 4-$MeOC_6H_4B(OH)_2$ (**7b**), 4-$F_3CC_6H_4B(OH)_2$ (**7c**) and 4-$PhC_6H_4B(OH)_2$ (**7d**). Some of the products possess interesting optical properties. More detailed spectroscopic studies on this new class of compound are currently underway in our laboratories.

Experimental Section

General Methods: Preparative column chromatography was carried out using Merck SiO_2 (0.035–0.070 mm, type 60 A) with petroleum ether (PE, boiling range 40–60 °C) and ethyl acetate (EA) as eluents. TLC was performed on Merck SiO_2 F_{254} plates on aluminium sheets. ^1H and ^{13}C NMR spectra were recorded with Bruker Avance DRX 500 and Avance DPX 300 spectrometers. Multiplicities were determined by DEPT experiments. EI-MS, CI-MS and HRMS spectra were obtained with a Finnigan MAT 95 spectrometer and ESI-MS spectra with a Waters Q-TOF Premier. IR spectra were recorded with a Bruker Tensor 27 spectrometer equipped with a "GoldenGate" diamond-ATR unit. Elemental analyses were measured with a Euro EA-CHNS instrument from HEKAtech. Esters **1** were prepared according to procedures reported previously.[3] All other starting materials were commercially available.

4-Iodo-4′-nitrobiphenyl (6): A solution of iodine (3.30 g, 13.0 mmol) in AcOH (15 mL) was added to biphenyl (**4**) (2.00 g, 13.0 mmol) and the mixture was stirred at 50 °C for 10 min. A mixture of concd. H_2SO_4 (6.37 g, 65.0 mmol) and concd. HNO_3 (65%, 3.20 g, 35.1 mmol) was slowly added dropwise. The reaction mixture was stirred for a further 2 h at 110 °C. Then KOH (30% solution in water, ca. 80 mL) was added at 0 °C. After separation of the phases, the aqueous phase was extracted three times with CH_2Cl_2 (each 50 mL). The organic phases were combined and dried with $MgSO_4$. After filtration the solvent was evaporated and the residue was recrystallized from PE/EtOAc (1:4, 50 mL). A yellow solid of an inseparable mixture (2.46 g) of 4-iodo-4′-nitrobiphenyl (**6**) (1.51 g, 4.64 mmol, 36%) and 4,4′-diiodobiphenyl (**5**) (0.95 g, 2.34 mmol, 18%) was obtained.

4-Iodo-4′-nitrobiphenyl (6): ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.30–7.50 (m, 2 H, 3,5-H), 7.58–7.72 (m, 2 H, 2,6-H), 7.81–7.95 (m, 2 H, 2′,6′-H), 8.20–8.40 (m, 2 H, 3′,5′-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 93.50 (C-4), 109.57 (C), 124.23 (2 CH), 127.59 (2 CH), 129.05 (2 CH), 138.31 (2 CH), 139.55 (C), 146.43 (C) ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 325 (100) $[M]^+$, 295 (32), 267 (19), 152 (93), 139 (26), 126 (16), 102 (7), 76 (27), 63 (23).

4,4′-Diiodobiphenyl (5): ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.20–7.30 (m, 4 H, 3,5-H, 3′,5′-H), 7.73–7.80 (m, 4 H, 2,6-H, 2′,6′-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 93.50 (C-4, C-4′), 128.67 (4 CH), 137.99 (4 CH), 139.55 (2 C) ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 406 (54) $[M]^+$, 280 (12), 203 (11), 152 (100), 126 (18), 102 (8), 76 (53), 63 (25).

4-Amino-4′-iodobiphenyl (2c): A solid mixture of 4-iodo-4′-nitrobiphenyl (**6**) and 4,4′-diiodobiphenyl (**5**) (3.25 g, ratio 2:1) was suspended in EtOH (20 mL). After addition of concd. hydrochloric acid (1 mL) the mixture was stirred at reflux for 10 min and then Zn powder (1.69 g, 25.8 mmol) was added in small portions. The mixture was stirred at reflux for another hour and then cooled to 23 °C, then hydrochloric acid (18%, 50 mL) was added slowly. The yellow solution was extracted with CH_2Cl_2 (3 × 50 mL). After separating and discarding the organic phase, the aqueous phase was neutralized with KOH (20% solution in water, ca. 80 mL). The precipitate was filtered off and discarded. The filtrate was extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were dried with $MgSO_4$ and filtered. After evaporation of the solvent 4-amino-4′-iodobiphenyl (**2c**) (1.32 g, 4.47 mmol, 73%) was obtained as a dark-yellow solid, m.p. 152–154 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 3.74 (br. s, 2 H, NH), 6.70–6.80 (m, 2 H, 3′,5′-H), 7.20–7.30 (m, 2 H, 2′,6′-H), 7.31–7.40 (m, 2 H, 2,6-H), 7.64–7.73 (m, 2 H, 3,5-H) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 91.49 (C-4′), 115.37 (2 CH), 127.77 (2 CH), 128.23 (2 CH), 130.21 (C), 137.66 (2 CH), 140.65 (C), 146.23 (C) ppm. IR (ATR): $\tilde{\nu}$ = 3407 (s), 3290 (s), 3189 (s), 3029 (m), 2983 (s), 1600 (s), 1519 (s), 1475 (s), 1389 (s), 1270 (s), 1201 (m), 1180 (m), 1139 (s), 1064 (s), 993 (s), 847 (s), 808 (vs) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 295 (100) $[M]^+$, 167 (18), 139 (6), 84 (11). HRMS: calcd. for $C_{12}H_{10}IN$ $[M]^+$ 294.9858; found 294.9857.

Diethyl 2,5-Bis(phenylamino)terephthalate (3a): Aniline (**2a**) (4.4 g, 4.3 mL, 47 mmol) and four drops of concd. hydrochloric acid were added to a solution of diethyl succinyl succinate **1a** (1.0 g, 3.9 mmol) in toluene (6 mL). The reaction mixture was stirred for 2 d at 60 °C and then concentrated under reduced pressure. The residue was purified by chromatography on Al_2O_3 [activity I, PE/CH_2Cl_2, 2:1, $R_f(SiO_2)$ = 0.23]. The crude product was recrystallized from PE/EtOAc (2:3, 25 mL) to yield **3a** (1.40 g, 3.46 mmol, 89%) as a red solid, m.p. 140 °C. The ^1H and ^{13}C NMR and IR data are in accordance with the literature.[12] MS (EI, 70 eV): *m*/*z* (%) = 404 (100) $[M]^+$, 312 (22), 284 (5), 255 (5). $C_{24}H_{24}N_2O_4$ (404.46): calcd. C 71.27, H 5.98, N 6.93; found C 70.94, H 5.95, N 6.94.

Dioctyl 2,5-Bis(phenylamino)terephthalate (3b): In analogy to the procedure reported for compound **3a**, aniline (**2a**) (5.3 g, 5.2 mL, 57 mmol), 10 drops of concd. hydrochloric acid, dioctyl succinyl succinate **1b** (2.00 g, 4.71 mmol) were allowed to react in toluene

(20 mL) to give product **3b** (2.48 g, 4.33 mmol, 92%) as an orange solid, m.p. 109 °C, after chromatography on Al_2O_3 [activity I, PE/CH_2Cl_2, 10:1, $R_f(SiO_2)$ = 0.45]. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.88 (t, J = 6.9 Hz, 6 H, CH_3), 1.21–1.34 (m, 16 H, CH_2), 1.38 (quint, J = 7.0 Hz, 4 H, CH_2), 1.69 (quint, J = 7.0 Hz, 4 H, CH_2), 4.25 (t, J = 6.5 Hz, 4 H, OCH_2), 6.93–7.03 (m, 2 H, 4′-H), 7.13–7.22 (m, 4 H, 2′,6′-H), 7.25–7.34 (m, 4 H, 3′,5′-H), 8.05 (s, 2 H, 3,6-H), 8.81 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.06 (CH_3), 22.62 (CH_2), 26.03 (CH_2), 28.52 (CH_2), 29.18 (CH_2), 29.20 (CH_2), 31.77 (CH_2), 65.26 (OCH_2), 118.43 (CH), 119.11 (C), 119.51 (2 CH), 121.86 (CH), 129.31 (2 CH), 137.71 (C), 142.06 (C), 167.49 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3347 (s), 3054 (w), 2954 (m), 2921 (s), 2852 (s), 1683 (vs), 1598 (s), 1585 (s), 1495 (s), 1436 (s), 1409 (vs), 1304 (m), 1252 (s), 1208 (vs), 1100 (s), 779 (s), 744 (s), 693 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 572 (100) $[M]^+$, 460 (4), 312 (10), 285 (4). $C_{36}H_{48}N_2O_4$ (572.79): calcd. C 75.49, H 8.45, N 4.89; found C 75.56, H 8.46, N 4.84.

Diethyl 2,5-Bis(4-iodophenylamino)terephthalate (3c): 4-Iodoaniline (**2b**) (5.13 g, 23.4 mmol) and three drops of concd. hydrochloric acid were added to a solution of diethyl succinyl succinate **1a** (500 mg, 1.95 mmol) in toluene (6 mL). The reaction mixture was stirred for 16 h at 60 °C. On cooling to 23 °C the crude product precipitated and was filtered off. Recrystallization from EtOAc (20 mL) yielded **3c** (1.10 g, 1.68 mmol, 86%) as a red solid, m.p. 209–210 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.36 (t, J = 7.1 Hz, 6 H, CH_3), 4.34 (q, J = 7.1 Hz, 4 H, OCH_2), 6.90–7.00 (m, 4 H, 2′,6′-H), 7.51–7.63 (m, 4 H, 3′,5′-H), 7.98 (s, 2 H, 3,6-H), 8.82 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.24 (CH_3), 61.50 (OCH_2), 83.66 (C-4′), 118.90 (CH), 119.69 (C), 121.07 (2 CH), 137.29 (C), 138.21 (2 CH), 141.93 (C), 167.27 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3337 (s), 3067 (w), 2984 (m), 1680 (vs), 1575 (s), 1535 (vs), 1477 (s), 1451 (s), 1428 (s), 1386 (s), 1247 (s), 1210 (vs), 1105 (s), 1062 (s), 1012 (s), 827 (s), 811 (s), 797 (s), 785 (s), 694 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 656 (100) $[M]^+$, 628 (3), 529 (6), 437 (3), 328 (4), 310 (20), 283 (6), 155 (4). HRMS: calcd. for $C_{24}H_{22}I_2N_2O_4$ $[M]^+$ 655.9669; found 655.9669.

Dioctyl 2,5-Bis(4-iodophenylamino)terephthalate (3d): In analogy to the procedure reported for compound **3a**, 4-iodoaniline (**2b**) (4.94 g, 22.6 mmol), four drops of concd. hydrochloric acid and dioctyl succinyl succinate **1b** (800 mg, 1.88 mmol) were allowed to react in toluene (10 mL) to give product **3d** (1.44 g, 1.75 mmol, 93%) as an orange solid, m.p. 143 °C, after chromatography on Al_2O_3 [activity I, PE/CH_2Cl_2, 2:1, $R_f(SiO_2)$ = 0.51]. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.89 (t, J = 6.7 Hz, 6 H, CH_3), 1.23–1.35 (m, 16 H, CH_2), 1.35–1.43 (m, 4 H, CH_2), 1.71 (quint, J = 6.8 Hz, 4 H, CH_2), 4.27 (t, J = 6.4 Hz, 4 H, OCH_2), 6.90–7.00 (m, 4 H, 2′,6′-H), 7.51–7.61 (m, 4 H, 3′,5′-H), 7.99 (s, 2 H, 3,6-H), 8.83 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.12 (CH_3), 22.66 (CH_2), 26.08 (CH_2), 28.54 (CH_2), 29.24 (2 CH_2), 31.81 (CH_2), 65.53 (OCH_2), 83.71 (C-4′), 118.65 (CH), 119.48 (C), 121.17 (2 CH), 137.29 (C), 138.17 (2 CH), 141.79 (C), 167.30 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3349 (s), 3066 (w), 2949 (m), 2922 (s), 2846 (s), 1679 (vs), 1584 (s), 1568 (s), 1525 (vs), 1486 (s), 1463 (s), 1424 (s), 1388 (s), 1251 (s), 1216 (vs), 1106 (s), 1003 (s), 830 (s), 795 (s), 783 (s), 725 (s), 696 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 824 (100) $[M]^+$, 698 (4), 310 (5). HRMS: calcd. for $C_{36}H_{46}I_2N_2O_4$ $[M]^+$ 824.1559; found 824.1546.

Diethyl 2,5-Bis(4′-iodobiphenyl-4-ylamino)terephthalate (3e): A mixture of diethyl succinyl succinate **1a** (180 mg, 702 μmol) and 4-amino-4′-iodobiphenyl (**2c**) (1.66 g, 5.62 mmol) was stirred in AcOH (15 mL) for 16 h at 100 °C. After cooling to ambient temperature, the precipitated product was filtered off, washed with CH_2Cl_2 (30 mL) and H_2O (20 mL) and dried in vacuo. The product **3e** (382 mg, 473 μmol, 67%) was obtained as a reddish-brown solid, m.p. 239 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.36 (t, J = 7.0 Hz, 6 H, CH_3), 4.35 (q, J = 7.1 Hz, 4 H, OCH_2), 7.20–7.29 (m, 4 H, 3′,5′-H), 7.30–7.36 (m, 4 H, 2′,6′-H), 7.48–7.55 (m, 4 H, 2′′,6′′-H), 7.70–7.79 (m, 4 H, 3′′,5′′-H), 8.11 (s, 2 H, 3,6-H), 8.93 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.26 (CH_3), 64.70 (OCH_2), 93.55 (C-4′), 118.29 (CH), 119.13 (C), 119.18 (2 CH), 127.77 (2 CH), 128.40 (2 CH), 133.76 (C), 137.80 (2 CH), 137.86 (C), 140.46 (C), 141.33 (C), 167.64 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3342 (s), 3034 (m), 2975 (s), 2927 (m), 1685 (vs), 1606 (s), 1578 (s), 1556 (s), 1530 (vs), 1476 (s), 1429 (s), 1403 (s), 1388 (m), 1369 (m), 1318 (s), 1283 (s), 1255 (s), 1208 (vs), 1180 (s), 1098 (vs), 1017 (s), 997 (s), 815 (s) cm^{-1}. MS (ESI): *m*/*z* (%) = 808 (100) $[M]^+$. HRMS: calcd. for $C_{36}H_{30}I_2N_2O_4$ $[M]^+$ 808.0295; found 808.0300.

Dioctyl 2,5-Bis(4′-iodobiphenyl-4-ylamino)terephthalate (3f): A mixture of dioctyl succinyl succinate **1b** (433 mg, 1.02 mmol) and 4-amino-4′-iodobiphenyl (**2c**) (3.01 g, 10.2 mmol) was stirred in AcOH (30 mL) for 16 h at 100 °C. After cooling to ambient temperature, the precipitate was isolated by filtration and washed with EtOAc (40 mL). Recrystallization from CH_2Cl_2 (80 mL) yielded **3f** (666 mg, 682 μmol, 67%) as a reddish-brown solid, m.p. 208 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.84 (t, J = 6.9 Hz, 6 H, CH_3), 1.13–1.26 (m, 12 H, CH_2), 1.26–1.35 (m, 4 H, CH_2), 1.40 (quint, J = 7.4 Hz, 4 H, CH_2), 1.72 (quint, J = 7.0 Hz, 4 H, CH_2), 4.30 (t, J = 6.5 Hz, 4 H, OCH_2), 7.20–7.28 (m, 4 H, 3′,5′-H), 7.29–7.35 (m, 4 H, 2′,6′-H), 7.45–7.55 (m, 4 H, 2′′,6′′-H), 7.68–7.77 (m, 4 H, 3′′,5′′-H), 8.12 (s, 2 H, 3,6-H), 8.95 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.10 (CH_3), 22.61 (CH_2), 26.10 (CH_2), 28.56 (CH_2), 29.26 (2 CH_2), 31.79 (CH_2), 65.46 (OCH_2), 92.14 (C-4′), 118.87 (CH), 119.30 (2 CH), 119.43 (C), 127.72 (2 CH), 128.35 (2 CH), 133.25 (C), 137.38 (C), 137.80 (2 CH), 140.23 (C), 141.82 (C), 167.42 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3312 (s), 3036 (m), 2952 (s), 2918 (s), 2848 (s), 1682 (vs), 1607 (s), 1584 (s), 1558 (s), 1538 (vs), 1478 (s), 1460 (s), 1434 (s), 1390 (m), 1326 (s), 1246 (s), 1216 (s), 1108 (s), 1067 (s), 1006 (s), 997 (s), 843 (s), 809 (s), 785 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 976 (100) $[M]^+$, 850 (7), 716 (4), 488 (3), 295 (4). HRMS: calcd. for $C_{48}H_{54}I_2N_2O_4$ $[M]^+$ 976.2173; found 976.2171.

Diethyl 2,5-Bis(biphenyl-4-ylamino)terephthalate (3g): A flame-dried Schlenk tube was filled under nitrogen with diethyl ester **3c** (150 mg, 229 μmol), $PhB(OH)_2$ (**7a**) (61 mg, 504 μmol), Na_2CO_3 (97 mg, 916 μmol) and $[Pd(PPh_3)_4]$ (13 mg, 11 μmol). Degassed solvent (toluene/EtOH, 1:1, 6 mL) was added dropwise followed by stirring for 30 min at 23 °C. Subsequently, degassed H_2O (4.5 mL) was added and the reaction mixture heated at reflux for 16 h. After cooling to ambient temperature, the precipitate was isolated by filtration, washed with EtOAc (20 mL) and H_2O (10 mL) and dried in vacuo. Compound **3g** (89 mg, 160 μmol, 70%) was obtained as a reddish-brown solid, m.p. 209 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.37 (t, J = 7.1 Hz, 6 H, CH_3), 4.36 (q, J = 7.1 Hz, 4 H, OCH_2), 7.22–7.29 (m, 4 H, 3′,5′-H), 7.29–7.37 (m, 2 H, 4′′-H), 7.39–7.48 (m, 4 H, 3′′,5′′-H), 7.54–7.65 (m, 8 H, 2′,6′-H, 2′′,6′′-H), 8.12 (s, 2 H, 3,6-H), 8.91 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.23 (CH_3), 61.35 (OCH_2), 119.00 (CH), 119.31 (2 CH), 119.51 (C), 126.58 (2 CH), 126.72 (CH), 127.99 (2 CH), 128.75 (2 CH), 134.57 (C), 137.51 (C), 140.77 (C), 141.54 (C), 167.45 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3342 (s), 3320 (s), 3034 (m), 2983 (s), 2904 (m), 1684 (vs), 1605 (m), 1573 (s), 1530 (vs), 1482 (s), 1421 (s), 1394 (s), 1314 (s), 1251 (s), 1209 (vs), 1091 (s), 1022 (s), 838 (s), 784 (s), 758 (s), 690 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 556 (100) $[M]^+$, 464 (20), 278 (7), 218 (3). HRMS: calcd. for $C_{36}H_{32}N_2O_4$ $[M]^+$ 556.2362; found 556.2361.

Dioctyl 2,5-Bis(biphenyl-4-ylamino)terephthalate (3h): In analogy to the procedure reported for compound **3g**, dioctyl ester **3d** (500 mg, 606 μmol), $PhB(OH)_2$ (**7a**) (163 mg, 1.33 mmol), Na_2CO_3 (257 mg, 2.42 mmol) and $[Pd(PPh_3)_4]$ (35 mg, 30 μmol) were allowed to react in degassed solvent (10 mL toluene, 10 mL EtOH, 5 mL H_2O). The precipitated product was isolated by filtration, washed with EtOAc (50 mL) and H_2O (30 mL) and dried in vacuo. Compound **3h** (215 mg, 297 μmol, 49%) was obtained as an orange solid, m.p. 206 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.84 (t, J = 6.6 Hz, 6 H, CH_3), 1.22–1.27 (m, 12 H, CH_2), 1.29–1.33 (m, 4 H, CH_2), 1.41 (quint, J = 7.2 Hz, 4 H, CH_2), 1.73 (quint, J = 7.0 Hz, 4 H, CH_2), 4.29 (t, J = 6.5 Hz, 4 H, OCH_2), 7.23–7.29 (m, 4 H, 3′,5′-H), 7.29–7.35 (m, 2 H, 4′′-H), 7.39–7.46 (m, 4 H, 3′′,5′′-H), 7.52–7.63 (m, 8 H, 2′,6′-H, 2′′,6′′-H), 8.13 (s, 2 H, 3,6-H), 8.92 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.06 (CH_3), 22.59 (CH_2), 26.09 (CH_2), 28.56 (CH_2), 29.24 (2 CH_2), 31.78 (CH_2), 65.41 (OCH_2), 118.78 (CH), 119.33 (C), 119.41 (2 CH), 126.55 (2 CH), 126.72 (CH), 127.95 (2 CH), 128.74 (2 CH), 134.62 (C), 137.53 (C), 140.75 (C), 141.42 (C), 167.51 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3309 (s), 3063 (m), 3031 (s), 2954 (s), 2921 (s), 2848 (s), 1685 (vs), 1607 (s), 1585 (s), 1572 (s), 1538 (vs), 1486 (s), 1463 (s), 1426 (s), 1398 (s), 1250 (s), 1209 (vs), 1105 (s), 834 (s), 785 (s), 758 (s), 690 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 724 (100) $[M]^+$, 464 (10), 437 (4), 362 (3), 168 (3). $C_{48}H_{56}N_2O_4$ (724.98): calcd. C 79.52, H 7.79, N 3.86; found C 79.78, H 7.92, N 3.58.

Diethyl 2,5-Bis(4′-methoxybiphenyl-4-ylamino)terephthalate (3i): In analogy to the procedure reported for compound **3g**, diethyl ester **3c** (150 mg, 229 μmol), $4\text{-}MeOC_6H_4B(OH)_2$ (**7b**) (77 mg, 504 μmol), Na_2CO_3 (97 mg, 916 μmol) and $[Pd(PPh_3)_4]$ (13 mg, 11 μmol) were allowed to react in degassed solvent (3 mL toluene, 3 mL EtOH, 4.5 mL H_2O). The precipitated product was isolated by filtration, washed with EtOAc (20 mL) and H_2O (10 mL) and dried in vacuo. Compound **3i** (59 mg, 96 μmol, 42%) was obtained as a brown solid, m.p. 265–269 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.36 (t, J = 7.1 Hz, 6 H, CH_3), 3.86 (s, 6 H, CH_3), 4.35 (q, J = 7.1 Hz, 4 H, OCH_2), 6.92–7.01 (m, 4 H, 3′,5′-H), 7.20–7.28 (m, 4 H, 3′′,5′′-H), 7.48–7.57 (m, 8 H, 2′,6′-H, 2′′,6′′-H), 8.09 (s, 2 H, 3,6-H), 8.87 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.24 (CH_3), 55.37 (CH_3), 61.31 (OCH_2), 114.12 (2 CH), 118.86 (CH), 119.40 (C), 119.51 (2 CH), 127.55 (2 CH), 127.60 (2 CH), 133.44 (C), 134.36 (C), 137.61 (C), 140.98 (C), 158.77 (C), 167.49 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3311 (s), 3030 (m), 2985 (s), 2941 (s), 2836 (s), 1682 (vs), 1604 (s), 1584 (m), 1572 (m), 1538 (s), 1495 (vs), 1431 (s), 1367 (s), 1320 (s), 1275 (s), 1240 (s), 1205 (vs), 1174 (m), 1093 (s), 819 (s), 784 (s), 689 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 616 (100) $[M]^+$, 524 (6), 262 (11). HRMS: calcd. for $C_{38}H_{36}N_2O_6$ $[M]^+$ 616.2573; found 616.2572.

Dioctyl 2,5-Bis(4′-methoxybiphenyl-4-ylamino)terephthalate (3j): In analogy to the procedure reported for compound **3g**, dioctyl ester **3d** (300 mg, 364 μmol), $4\text{-}MeOC_6H_4B(OH)_2$ (**7b**) (122 mg, 801 μmol), Na_2CO_3 (154 mg, 1.46 mmol) and $[Pd(PPh_3)_4]$ (21 mg, 18 μmol) were allowed to react in degassed solvent (4 mL toluene, 4 mL EtOH, 5 mL H_2O). The precipitated product was isolated by filtration, washed with CH_2Cl_2 (30 mL) and H_2O (30 mL) and dried in vacuo. Compound **3j** (120 mg, 153 μmol, 42%) was obtained as a red solid, m.p. 208–209 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.77 (t, J = 6.9 Hz, 6 H, CH_3), 1.00–1.27 (m, 16 H, CH_2), 1.28–1.38 (m, 4 H, CH_2), 1.65 (quint, J = 6.9 Hz, 4 H, CH_2), 3.78 (s, 6 H, OCH_3), 4.21 (t, J = 6.5 Hz, 4 H, OCH_2), 6.80–7.00 (m, 4 H, 3′,5′-H), 7.08–7.26 (m, 4 H, 3′′,5′′-H), 7.30–7.62 (m, 8 H, 2′,6′-H, 2′′,6′′-H), 8.04 (s, 2 H, 3,6-H), 8.82 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.08 (CH_3), 22.60 (CH_2), 26.09 (CH_2), 28.56 (CH_2), 29.26 (2 CH_2), 31.80 (CH_2), 55.35 (CH_3), 65.36 (OCH_2), 114.19 (2 CH), 118.62 (CH), 119.19 (C), 119.61 (2 CH), 127.50 (2 CH), 127.57 (2 CH), 133.45 (C), 134.42 (C), 137.63 (C), 140.86 (C), 158.77 (C), 167.54 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3311 (s), 3010 (m), 2957 (s), 2918 (s), 2847 (s), 1683 (vs), 1607 (s), 1586 (s), 1575 (m), 1543 (vs), 1496 (s), 1456 (s), 1434 (s), 1397 (m), 1330 (vs), 1276 (s), 1212 (vs), 1175 (s), 1107 (s), 822 (s), 783 (s), 689 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 784 (100) $[M]^+$, 392 (3), 392 (4), 198 (4). HRMS: calcd. for $C_{50}H_{60}N_2O_6$ $[M]^+$ 784.4451; found 784.4451.

Diethyl 2,5-Bis[4′-(trifluoromethyl)biphenyl-4-ylamino]terephthalate (3k): In analogy to the procedure reported for compound **3g**, diethyl ester **3c** (150 mg, 229 μmol), $4\text{-}F_3CC_6H_4B(OH)_2$ (**7c**) (96 mg, 504 μmol), Na_2CO_3 (97 mg, 916 μmol) and $[Pd(PPh_3)_4]$ (13 mg, 11 μmol) were allowed to react in degassed solvent (6 mL toluene, 3 mL EtOH, 4.5 mL H_2O). The precipitated product was isolated by filtration, washed with CH_2Cl_2 (20 mL) and H_2O (10 mL) and dried in vacuo. Compound **3k** (87 mg, 126 μmol, 55%) was obtained as a brownish-yellow solid, m.p. 286–287 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.38 (t, J = 7.1 Hz, 6 H, CH_3), 4.30 (q, J = 7.1 Hz, 4 H, OCH_2), 7.28–7.38 (m, 4 H, 3′,5′-H), 7.50–7.62 (m, 4 H, 3′′,5′′-H), 7.62–7.75 (m, 8 H, 2′,6′-H, 2′′,6′′-H), 8.14 (s, 2 H, 3,6-H), 8.98 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.25 (CH_3), 61.47 (OCH_2), 119.06 (2 CH), 119.27 (CH), 119.77 (C), 125.71 (q, ^3J = 3.2 Hz, 2 CH, C-3′′, C-5′′), 126.08 (q, ^1J = 247.7 Hz, 1 C, CF_3), 126.67 (2 CH), 128.20 (2 CH), 130.11 (q, ^2J = 30.7 Hz, 1 C, C-4′′), 134.03 (C), 135.65 (C), 142.39 (C), 144.47 (C), 167.35 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3343 (s), 3042 (m), 2983 (s), 1685 (vs), 1602 (s), 1585 (s), 1567 (s), 1527 (vs), 1501 (s), 1475 (s), 1431 (s), 1399 (m), 1324 (vs), 1278 (s), 1256 (s), 1210 (s), 1169 (s), 1113 (s), 1071 (vs), 1012 (s), 827 (s), 784 (s), 726 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 692 (100) $[M]^+$, 673 (4), 600 (25), 572 (4), 346 (4). HRMS: calcd. for $C_{38}H_{30}F_6N_2O_4$ $[M]^+$ 692.2110; found 692.2111.

Dioctyl 2,5-Bis[4′-(trifluoromethyl)biphenyl-4-ylamino]terephthalate (3l): In analogy to the procedure reported for compound **3g**, dioctyl ester **3d** (300 mg, 364 μmol), $4\text{-}F_3CC_6H_4B(OH)_2$ (**7c**) (152 mg, 801 μmol), Na_2CO_3 (154 mg, 1.46 mmol) and $[Pd(PPh_3)_4]$ (21 mg, 18 μmol) were allowed to react in degassed solvent (4 mL toluene, 4 mL EtOH, 5 mL H_2O). The precipitated product was isolated by filtration, washed with CH_2Cl_2 (30 mL) and H_2O (30 mL) and dried in vacuo. Compound **3l** (177 mg, 206 μmol, 57%) was obtained as a reddish-brown solid, m.p. 222–223 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.86 (t, J = 6.8 Hz, 6 H, CH_3), 1.18–1.28 (m, 12 H, CH_2), 1.28–1.38 (m, 4 H, CH_2), 1.45 (quint, J = 7.4 Hz, 4 H, CH_2), 1.77 (quint, J = 7.0 Hz, 4 H, CH_2), 4.30 (t, J = 6.4 Hz, 4 H, OCH_2), 7.28–7.32 (m, 4 H, 3′,5′-H), 7.57–7.64 (m, 4 H, 3′′,5′′-H), 7.65–7.77 (m, 8 H, 2′,6′-H, 2′′,6′′-H), 8.19 (s, 2 H, 3,6-H), 9.03 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.46 (CH_3), 23.03 (CH_2), 26.57 (CH_2), 29.02 (CH_2), 29.72 (2 CH_2), 32.23 (CH_2), 65.96 (OCH_2), 119.46 (CH), 119.63 (2 CH), 120.02 (C), 124.80 (q, ^1J = 271.4 Hz, 1 C, CF_3), 126.14 (q, ^3J = 3.8 Hz, 2 CH, C-3′′, C-5′′), 127.07 (2 CH), 128.59 (2 CH), 129.15 (q, ^2J = 32.3 Hz, 1 C, C-4′′), 133.26 (C), 137.76 (C), 142.73 (C), 144.59 (C), 167.83 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3313 (s), 3009 (m), 2955 (s), 2917 (s), 2848 (s), 1683 (vs), 1607 (s), 1588 (s), 1574 (s), 1541 (vs), 1503 (s), 1460 (s), 1435 (s), 1397 (m), 1325 (vs), 1247 (s), 1218 (m), 1165 (s), 1072 (vs), 1014 (s), 824 (s), 787 (s), 723 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 860 (100) $[M]^+$, 731 (2), 600 (9), 366 (3). HRMS: calcd. for $C_{50}H_{54}F_6N_2O_4$ $[M]^+$ 860.3988; found 860.3987.

Diethyl 2,5-Bis(1,1′:4′,1′′-terphenyl-4-ylamino)terephthalate (3m): In analogy to the procedure reported for compound **3g**, diethyl ester **3c** (300 mg, 457 μmol), $4\text{-}PhC_6H_4B(OH)_2$ (**7d**) (200 mg,

1.01 mmol), Na_2CO_3 (194 mg, 1.83 mmol) and $[Pd(PPh_3)_4]$ (27 mg, 23 μmol) were allowed to react in degassed solvent (6 mL toluene, 6 mL EtOH, 9 mL H_2O). The precipitated product was isolated by filtration, washed with EtOAc (60 mL) and H_2O (60 mL) and dried in vacuo. Compound **3m** (49 mg, 206 μmol, 54%) was obtained as a red solid, m.p. 329–331 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.38 (t, J = 7.1 Hz, 6 H, CH_3), 4.37 (q, J = 7.1 Hz, 4 H, OCH_2), 7.28–7.30 (m, 4 H, 3′,5′-H), 7.32–7.40 (m, 2 H, 4′′′-H), 7.42–7.52 (m, 4 H, 3′′,5′′-H), 7.62–7.73 (m, 16 H, 2′,6′-H, 2′′,6′′-H, 3′′,5′′-H, 2′′′,6′′′-H), 8.14 (s, 2 H, 3,6-H), 8.94 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.72 (CH_3), 61.38 (OCH_2), 118.88 (CH), 119.10 (2 CH), 119.30 (C), 126.85 (2 CH), 126.98 (2 CH), 127.24 (CH), 127.33 (2 CH), 127.91 (2 CH), 128.75 (2 CH), 132.66 (C), 133.66 (C), 139.57 (C), 140.26 (C), 140.79 (C), 141.64 (C), 167.58 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3343 (s), 3042 (m), 2983 (s), 1685 (vs), 1602 (s), 1585 (s), 1567 (s), 1527 (vs), 1501 (s), 1475 (s), 1431 (s), 1399 (m), 1324 (vs), 1278 (s), 1256 (s), 1210 (s), 1169 (s), 1113 (s), 1071 (vs), 1012 (s), 827 (s), 784 (s), 726 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 708 (75) $[M]^+$, 616 (8), 556 (90), 464 (14), 354 (4), 306 (11), 266 (30), 232 (4), 105 (5), 91 (13), 44 (100). HRMS: calcd. for $C_{48}H_{40}N_2O_4$ $[M]^+$ 708.2988; found 708.2988.

Dioctyl 2,5-Bis(1,1′:4′,1′′-terphenyl-4-ylamino)terephthalate (3n): In analogy to the procedure reported for compound **3g**, dioctyl ester **3d** (300 mg, 364 μmol), 4-$PhC_6H_4B(OH)_2$ (**7d**) (159 mg, 801 μmol), Na_2CO_3 (154 mg, 1.46 mmol) and $[Pd(PPh_3)_4]$ (21 mg, 18 μmol) were allowed to react in degassed solvent (4 mL toluene, 4 mL EtOH, 5 mL H_2O). The precipitated product was isolated by filtration, washed with CH_2Cl_2 (20 mL) and H_2O (20 mL) and dried in vacuo. Compound **3n** (221 mg, 262 μmol, 72%) was obtained as a reddish-brown solid, m.p. 239–242 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.83 (t, J = 6.8 Hz, 6 H, CH_3), 1.18–1.29 (m, 12 H, CH_2), 1.28–1.38 (m, 4 H, CH_2), 1.39–1.47 (m, 4 H, CH_2), 1.74 (quint, J = 7.0 Hz, 4 H, CH_2), 4.30 (t, J = 6.5 Hz, 4 H, OCH_2), 7.28–7.32 (m, 4 H, 3′,5′-H), 7.33–7.39 (m, 2 H, 4′′′-H), 7.43–7.49 (m, 4 H, 3′′′,5′′′-H), 7.56–7.75 (m, 16 H, 2′,6′-H, 2′′,6′′-H, 3′′,5′′-H, 2′′′,6′′′-H), 8.15 (s, 2 H, 3,6-H), 8.96 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.09 (CH_3), 22.61 (CH_2), 26.12 (CH_2), 28.58 (CH_2), 29.28 (2 CH_2), 31.81 (CH_2), 65.82 (OCH_2), 118.70 (CH), 119.37 (C), 119.41 (2 CH), 126.84 (2 CH), 126.98 (2 CH), 127.23 (CH), 127.48 (2 CH), 127.84 (2 CH), 128.79 (2 CH), 133.07 (C), 134.02 (C), 139.35 (C), 140.79 (C), 141.16 (C), 141.19 (C), 167.83 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3304 (s), 3064 (m), 3029 (m), 2953 (s), 2919 (s), 2849 (s), 1684 (vs), 1607 (m), 1584 (s), 1558 (s), 1539 (s), 1504 (m), 1482 (s), 1462 (s), 1432 (s), 1398 (s), 1327 (s), 1298 (s), 1244 (s), 1207 (m), 1106 (s), 1054 (m), 1003 (m), 823 (s), 785 (s), 762 (s), 726 (s), 691 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 876 (25) $[M]^+$, 404 (4), 366 (12), 306 (65), 188 (52), 91 (83), 44 (100). HRMS: calcd. for $C_{60}H_{64}N_2O_4$ $[M]^+$ 876.4866; found 876.4870.

Diethyl 2,5-Bis(4′′-methoxy-1,1′:4′,1′′-terphenyl-4-ylamino)terephthalate (3o): In analogy to the procedure reported for compound **3g**, diethyl ester **3e** (150 mg, 186 μmol), 4-$MeOC_6H_4B(OH)_2$ (**7b**) (62 mg, 409 μmol), Na_2CO_3 (79 mg, 744 μmol) and $[Pd(PPh_3)_4]$ (11 mg, 9.3 μmol) were allowed to react in degassed solvent (3 mL toluene, 3 mol EtOH, 4.5 mL H_2O). The precipitated product was isolated by filtration, washed with CH_2Cl_2 (30 mL) and H_2O (30 mL) and dried in vacuo. Compound **3o** (86 mg, 112 μmol, 60%) was obtained as a brown solid, m.p. >350 °C. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.37 (t, J = 7.1 Hz, 6 H, CH_3), 3.87 (s, 6 H, OCH_3), 4.37 (q, J = 7.1 Hz, 4 H, OCH_2), 6.90–7.08 (m, 4 H, 3′,5′-H), 7.20–7.32 (m, 4 H, 3′′′,5′′′-H), 7.36–7.70 (m, 16 H, 2′,6′-H, 2′′,6′′-H, 3′′,5′′-H, 2′′′,6′′′-H), 8.13 (s, 2 H, 3,6-H), 8.93 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ = 14.12 (CH_3), 55.40 (OCH_3), 61.30 (OCH_2), 114.26 (2 CH), 118.72 (CH), 119.24 (C), 119.33 (2 CH), 126.83 (2 CH), 127.01 (CH), 127.04 (2 CH), 127.82 (2 CH), 127.99 (2 CH), 133.88 (C), 137.91 (C), 139.02 (C), 140.60 (C), 141.06 (C), 154.00 (C), 167.50 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3331 (s), 3031 (m), 2982 (m), 2939 (m), 2906 (m), 2837 (s), 1685 (vs), 1607 (s), 1582 (s), 1558 (m), 1540 (vs), 1491 (s), 1456 (m), 1435 (s), 1399 (s), 1370 (s), 1316 (s), 1292 (s), 1248 (s), 1208 (s), 1188 (s), 1099 (s), 814 (s), 784 (s), 717 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 768 (100) $[M]^+$, 677 (40), 546 (57), 384 (21), 339 (7), 275 (21), 259 (63), 215 (11), 44 (4). HRMS: calcd. for $C_{50}H_{44}N_2O_6$ $[M]^+$ 768.3199; found 768.3198.

Dioctyl 2,5-Bis(4′′-methoxy-1,1′:4′,1′′-terphenyl-4-ylamino)terephthalate (3p): In analogy to the procedure reported for compound **3g**, dioctyl ester **3f** (150 mg, 154 μmol), 4-$MeOC_6H_4B(OH)_2$ (**7b**) (52 mg, 339 μmol), Na_2CO_3 (65 mg, 616 μmol) and $[Pd(PPh_3)_4]$ (9 mg, 7.7 μmol) were allowed to react in degassed solvent (2 mL toluene, 2 mL EtOH, 3 mL H_2O). The precipitated product was isolated by filtration, washed with EtOAc (10 mL) and H_2O (10 mL) and dried in vacuo. Compound **3p** (123 mg, 131 μmol, 85%) was obtained as a brown solid, m.p. 239–241 °C. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.83 (t, J = 6.4 Hz, 6 H, CH_3), 1.08–1.20 (m, 12 H, CH_2), 1.20–1.30 (m, 4 H, CH_2), 1.31–1.40 (quint, J = 7.3 Hz, 4 H, CH_2), 1.65 (quint, J = 7.0 Hz, 4 H, CH_2), 3.87 (s, 6 H, OCH_3), 4.30 (t, J = 6.5 Hz, 4 H, OCH_2), 6.85–7.00 (m, 4 H, 3′,5′-H), 7.18–7.28 (m, 4 H, 3′′′,5′′′-H), 7.36–7.70 (m, 16 H, 2′,6′-H, 2′′,6′′-H, 3′′,5′′-H, 2′′′,6′′′-H), 8.07 (s, 2 H, 3,6-H), 8.79 (s, 2 H, NH) ppm. $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 14.09 (CH_3), 22.61 (CH_2), 26.11 (CH_2), 28.57 (CH_2), 29.26 (2 CH_2), 31.80 (CH_2), 55.37 (OCH_3), 65.43 (OCH_2), 114.26 (2 CH), 118.79 (CH), 119.33 (C), 119.42 (2 CH), 126.81 (2 CH), 127.02 (2 CH), 127.06 (CH), 127.77 (2 CH), 127.97 (2 CH), 133.32 (C), 134.12 (C), 139.02 (C), 139.16 (C), 141.41 (C), 159.16 (C), 167.50 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3308 (s), 3030 (m), 2954 (m), 2918 (s), 2849 (s), 1684 (vs), 1606 (s), 1582 (s), 1557 (m), 1538 (vs), 1488 (s), 1463 (s), 1433 (s), 1326 (s), 1330 (s), 1295 (s), 1245 (s), 1209 (vs), 1184 (s), 1105 (s), 811 (s), 785 (s), 712 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 936 (63) $[M]^+$, 830 (28), 676 (4), 468 (16), 366 (10), 275 (23), 244 (9), 71 (18), 57 (29), 44 (100). HRMS: calcd. for $C_{62}H_{68}N_2O_6$ $[M]^+$ 936.5077; found 936.5088.

Diethyl 2,5-Bis[4′′-(trifluoromethyl)-1,1′:4′,1′′-terphenyl-4-ylamino]-terephthalate (3q): In analogy to the procedure reported for compound **3g**, diethyl ester **3e** (127 mg, 157 μmol), 4-$F_3CC_6H_4B(OH)_2$ (**7c**) (66 mg, 345 μmol), Na_2CO_3 (67 mg, 628 μmol) and $[Pd(PPh_3)_4]$ (9 mg, 7.9 μmol) were allowed to react in degassed solvent (2 mL toluene, 2 mL EtOH, 3 mL H_2O). The precipitated product was isolated by filtration, washed with CH_2Cl_2 (35 mL) and H_2O (30 mL) and dried in vacuo. Compound **3q** (81 mg, 96 μmol, 61%) was obtained as a reddish-brown solid, m.p. >330 °C. Owing to insufficient solubility of **3q**, no NMR spectra could be obtained. IR (ATR): $\tilde{\nu}$ = 3336 (s), 3034 (m), 2983 (m), 1685 (vs), 1597 (s), 1581 (m), 1556 (m), 1530 (s), 1492 (s), 1455 (m), 1433 (s), 1398 (s), 1370 (m), 1324 (vs), 1253 (s), 1209 (s), 1170 (m), 1099 (vs), 1072 (vs), 1002 (s), 816 (vs), 787 (s) cm^{-1}. MS (ESI): m/z = 844 $[M]^+$. HRMS: calcd. for $C_{50}H_{38}F_6N_2O_4$ $[M]^+$ 844.2736; found 844.2732.

Dioctyl 2,5-Bis[4′′-(trifluoromethyl)-1,1′:4′,1′′-terphenyl-4-ylamino]-terephthalate (3r): In analogy to the procedure reported for compound **3g**, dioctyl ester **3f** (150 mg, 154 μmol), 4-$F_3CC_6H_4B(OH)_2$ (**7c**) (64 mg, 339 μmol), Na_2CO_3 (65 mg, 616 μmol) and $[Pd(PPh_3)_4]$ (9 mg, 7.7 μmol) were allowed to react in degassed solvent (2 mL toluene, 2 mL EtOH, 3 mL H_2O). The precipitated product was isolated by filtration, washed with EtOAc (15 mL) and H_2O (10 mL) and dried in vacuo. Compound **3r** (113 mg, 112 μmol,

73%) was isolated as a reddish-brown solid, m.p. 253–255 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.83 (t, J = 6.5 Hz, 6 H, CH_3), 1.15–1.28 (m, 12 H, CH_2), 1.28–1.37 (m, 4 H, CH_2), 1.38–1.64 (m, 4 H, CH_2), 1.69–1.78 (m, 4 H, CH_2), 4.30 (t, J = 6.4 Hz, 4 H, OCH_2), 7.27–7.32 (m, 4 H, 3′,5′-H), 7.42–7.50 (m, 4 H, 3‴,5‴-H), 7.52–7.63 (m, 16 H, 2′,6′-H, 2″,6″-H, 3″,5″-H, 2‴,6‴-H), 8.15 (s, 2 H, 3,6-H), 8.95 (s, 2 H, NH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ = 14.09 (CH_3), 22.60 (CH_2), 26.12 (CH_2), 28.56 (CH_2), 29.26 (2 CH_2), 31.80 (CH_2), 65.46 (OCH_2), 118.95 (CH), 119.23 (2 CH), 119.48 (CH), 119.50 (CH), 120.58 (C), 125.75 (q, ^3J = 3.8 Hz, 2 CH, C-3‴, C-5‴), 127.64 (q, ^1J = 275.5 Hz, 1 C, CF_3), 127.01 (2 CH), 127.62 (2 CH), 127.89 (2 CH), 128.30 (q, ^2J = 39.8 Hz, 1 C, C-4‴), 131.90 (C), 134.86 (C), 139.80 (C), 141.19 (C), 142.40 (C), 144.27 (C), 167.42 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3312 (s), 3035 (m), 2955 (m), 2920 (s), 2851 (s), 1684 (vs), 1606 (s), 1585 (s), 1560 (s), 1543 (s), 1494 (s), 1461 (s), 1436 (s), 1401 (s), 1328 (vs), 1249 (s), 1211 (s), 1168 (s), 1109 (vs), 1074 (vs), 1004 (s), 817 (vs), 787 (s) cm^{-1}. MS (ESI): m/z = 1012 $[M]^+$. HRMS: calcd. for $C_{62}H_{62}F_6N_2O_4$ 4619 $[M]^+$ 1012.4614; found 1012.4619.

Dioctyl 2,5-Bis(1,1′:4′,1″:4″,1‴-quaterphenyl-4-ylamino)terephthalate (3s): In analogy to the procedure reported for compound **3g**, dioctyl ester **3f** (150 mg, 154 μmol), 4-$PhC_6H_4B(OH)_2$ (**7d**) (67 mg, 338 μmol), Na_2CO_3 (65 mg, 616 μmol) and $[Pd(PPh_3)_4]$ (9 mg, 7.7 μmol) were allowed to react in degassed solvent (3 mL toluene, 3 mL EtOH, 4.5 mL H_2O). The precipitated product was isolated by filtration, washed with CH_2Cl_2 (20 mL) and H_2O (20 mL) and dried in vacuo. Compound **3s** (67 mg, 65 μmol, 42%) was obtained as a reddish-brown solid, m.p. 272 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.83 (t, J = 6.5 Hz, 6 H, CH_3), 1.12–1.32 (m, 16 H, CH_2), 1.36–1.48 (m, 4 H, CH_2), 1.67–1.80 (m, 4 H, CH_2), 4.30 (t, J = 6.0 Hz, 4 H, OCH_2), 7.27–7.32 (m, 4 H, 3′,5′-H), 7.34–7.42 (m, 2 H, 4‴′-H), 7.42–7.50 (m, 4 H, 3‴′,5‴′-H), 7.62–7.77 (m, 24 H, 2′,6′-H, 2″,6″-H, 3″,5″-H, 2‴,6‴-H, 3‴,5‴-H, 2‴′,6‴′-H), 8.15 (s, 2 H, 3,6-H), 8.92–9.01 (m, 2 H, NH) ppm. ^{13}C{^{1}H} NMR (125 MHz $CDCl_3$): δ = 14.10 (CH_3), 22.61 (CH_2), 26.11 (CH_2), 28.57 (CH_2), 29.27 (2 CH_2), 31.80 (CH_2), 65.45 (OCH_2), 115.72 (2 CH), 117.32 (C), 118.76 (CH), 126.67 (2 CH), 127.15 (CH), 127.33 (2 CH), 127.36 (2 CH), 127.48 (4 CH), 127.54 (2 CH), 128.73 (2 CH), 132.85 (C), 135.21 (C), 140.12 (2 C), 140.22 (C), 140.70 (C), 141.23 (C), 153.72 (C), 167.44 (C=O) ppm. IR (ATR): $\tilde{\nu}$ = 3308 (s), 3030 (m), 2961 (m), 2921 (s), 2849 (s), 1684 (vs), 1602 (s), 1532 (vs), 1479 (s), 1429 (s), 1396 (s), 1322 (s), 1293 (s), 1250 (s), 1207 (vs), 1101 (s), 999 (s), 813 (vs), 761 (s) cm^{-1}. MS (ESI): m/z = 1028 $[M]^+$. HRMS: calcd. for $C_{72}H_{72}N_2O_4$ $[M]^+$ 1028.5492; found 1028.5498.

Supporting Information (see also the footnote on the first page of this article): Details of crystal structure analysis, spectroscopy, as well as all of the absorption and emission spectra.

Acknowledgments

This work was generously supported by the Fonds der Chemischen Industrie. We are grateful to Ing. Halina Trelińska for recording the absorption spectra and Dr. Herbert Frey for his assistance in preparing this manuscript.

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Received: February 25, 2008
Published Online: May 30, 2008

