Benzothiadiazoloperylenes and Benzoxadiazoloperylenes: Amorphous Functional Materials

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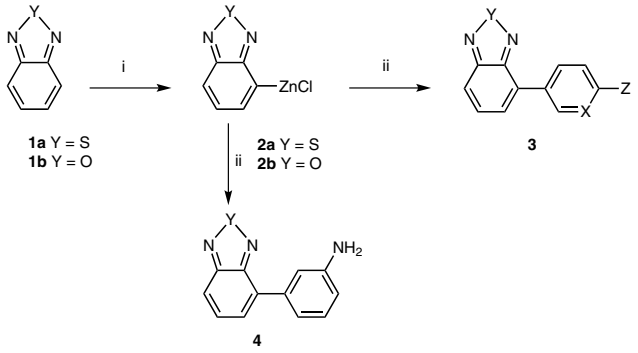
Abstract: 2,1,3-Benzothiadiazole or 2,1,3-benzoxadiazole were magnesiated ($TMP_2Mg·2LiCl$) and efficiently attached to perylene and benzoperylene building blocks providing amorphous light-absorbing materials where FRET energy transfer proceeds between the 2,1,3-benzothiadiazole or 2,1,3-benzoxadiazole and the perylene units. Some of these new materials were obtained as amorphous solids of interest for material science.

Key words: arenes, heterocycles, imides, cross-coupling fused-ring systems, zinc

Organic functional materials with special electronic and optical properties are of increasing interest in science and technology;[1] their variability and saving of resources are important features. Organic light emitting diodes (OLEDS) and organic photovoltaic devices based on extended π-systems of polycyclic aromatic or heteroaromatic compounds are very promising and much research activity is focused on perylenetetracarboxylic bisimides[2,3] because of their high chemical and photochemical stability.[4,5] However, their tendency for crystallization is problematic for such functional materials, since the molecular packing invariably determined by the crystal lattice is hard to predict and cannot be continuously altered. Moreover, there are interfering border effects between the crystallites. The availability of amorphous organic materials[6] would solve these problems. Herein, we wish to report the synthesis of such new amorphous materials bearing a perylene or benzoperylene moiety attached to 2,1,3-benzothiadiazole and 2,1,3-benzoxadiazole units, respectively, as well as their interesting optical properties.

We started the synthesis with 2,1,3-benzothiadiazole (**1a**) and 2,1,3-benzoxadiazole (**1b**) and prepared the novel zinc reagents **2a** and **2b**,[7] respectively, by direct magnesiation with bis(2,2,6,6-tetramethylpiperidin-1-yl)magnesium–lithium chloride complex[8] ($TMP_2Mg·2LiCl$) in tetrahydrofuran (1.4 equiv, –40 °C or –5 °C, 14 h) followed by transmetalation with zinc chloride (1.5 equiv, –40 °C or –5 °C, 0.5 h) in ca. 85% yields (Scheme 1). Further palladium-mediated cross-coupling of **2a** [$Pd(dba)_2$ (2 mol%), $(2\text{-furyl})_3P$ (4 mol%)] and of **2b** [$Pd(OAc)_2$ (2 mol%), SPhos[9] (4 mol%), 21 °C, 24 h] with iodobenzene provided the reference materials **3a** and **3b** (Table 1, entries 3 and 4). Cross-coupling of 4-iodoaniline, 5-iodopyridin-2-amine, or 3-iodoaniline allowed the preparation of the amino derivatives **3c**–**f** and **4a**,**b**, respectively, with amino groups for the condensation with carboxylic anhydrides (entries 5–8, 1 and 2). Finally, **3g** was prepared from 1-iodo-4-(trimethylsilyl)benzene and was further converted into **3h** by means of iodine monochloride to become the starting material for subsequent cross-coupling reactions (entries 9 and 10).



Scheme 1 Synthesis of 2,1,3-benzothiadiazoles and 2,1,3-benzoxadiazoles, respectively. *Reagents and conditions:* (i) 1. $(TMP)_2Mg·2LiCl$, THF; 2. $ZnCl_2$; (ii) see Table 1.

The amino derivatives **3c**–**f** were condensed with the perylene anhydride carboximides **5a** and **5b** to form the perylenetetracarboxylic bisimides **6a**,**e** and **7a** where the long-chain secondary alkyl substituents increases the solubility of the materials and 1-nonyldecyl is more efficient than the 1-hexylheptyl substituent (Scheme 2, Table 2).

The benzoperylene derivatives **8** were condensed in the same manner. Alternatively, 4-iodoaniline and 2-amino-5-iodopyridine were condensed with the anhydrides **5** and **8**, respectively, and further cross-coupled with **2a** [$Pd(dba)_2$ (2 mol%), $(furyl)_3P$[10] (4 mol%), 20 °C, 24 h] to form the dyads **6a**, **6e** and **9a** (Scheme 3), however, the yields were slightly lower (47%, 52%, and 29% yield, respectively, over two steps) than for the condensation of the corresponding anhydrides with amines (70%, 72%, and 75%). The benzoxadiazole derivatives **6c**, **6d**, **7a**, **9b**, and **10a** were prepared in the same way by the condensation of the corresponding amines with the anhydrides **5** or **8**. Finally, the zinc compound **2a** was cross-coupled with the bromoperylenedicarboxylic imide **11** to form **12**

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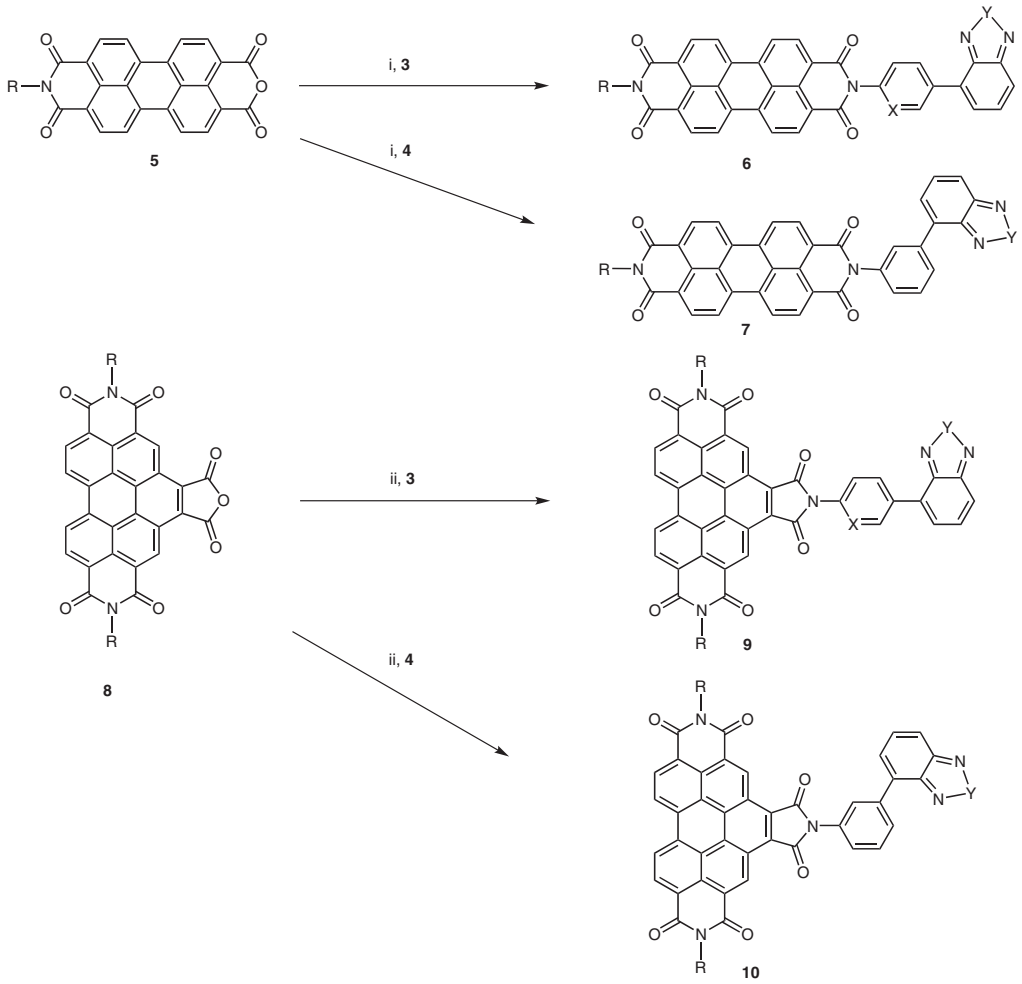
Table 1 Conditions for the Formation of **3a**–**h**, **4a**,**b**

Entry	X	Y	Z	Conditions	Product	Yield (%)
1	–	S	–	**2a**, 3-iodoaniline, $Pd(OAc)_2$, SPhos, THF	**4a**	61
2	–	O	–	**2b**, 3-iodoaniline, $Pd(OAc)_2$, SPhos, THF	**4b**	55
3	CH	S	H	**2a**, PhI, $Pd(dba)_2$, $(2\text{-furyl})_3P$, THF	**3a**	83
4	CH	O	H	**2b**, $Pd(OAc)_2$, SPhos, PhI, THF	**3b**	69
5	CH	S	NH_2	**2a**, 4-iodoaniline, $Pd(OAc)_2$, SPhos, THF	**3c**	61
6	CH	O	NH_2	**2b**, 4-iodoaniline, $Pd(OAc)_2$, SPhos, THF	**3d**	59
7	N	S	NH_2	**2a**, 5-iodopyridin-2-amine, $Pd(OAc)_2$, SPhos, THF	**3e**	53
8	N	O	NH_2	**2b**, 5-iodopyridin-2-amine, $Pd(OAc)_2$, SPhos, THF	**3f**	54
9	CH	S	TMS	**2a**, (4-bromophenyl)trimethylsilane, $Pd(dba)_2$, $(furyl)_3P$, THF	**3g**	42
10	CH	S	I	from **3g**: ICl, CH_2Cl_2	**3h**	93

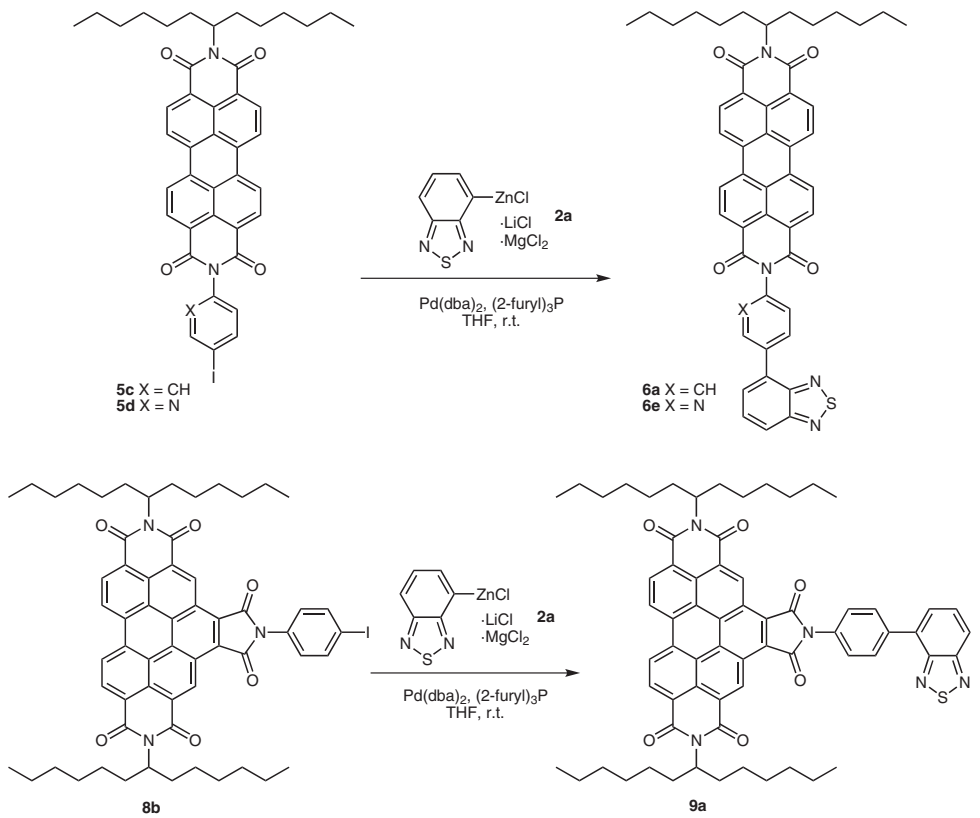


Scheme 2 Synthesis of 2,1,3-benzothiadiazoloperylenes (see Table 2). *Reagents and conditions:* (i) $Zn(OAc)_2$, quinoline, 210 °C, 5 h; (ii) $Zn(OAc)_2$, microwaves.

Table 2 Condensation of Perylene Anhydrides

Entry	Compound	X	Y	R	Substrates	Conditions	Yield (%)	Crystallinity
1	**5a**	–	–	$CH(C_6H_{13})_2$	–	–	–	crystalline
2	**5b**	–	–	$CH(C_9H_{18})_2$	–	–	–	crystalline
3	**6a**	CH	S	$CH(C_6H_{13})_2$	–[a]	$Pd(dba)_2$, (2-furyl)$_3$P, THF	60	amorphous
4	**6b**	CH	S	$CH(C_9H_{18})_2$	**3c** + **5b**	$Zn(OAc)_2$, quinoline, 210 °C	74	amorphous
5	**6c**	CH	O	$CH(C_6H_{13})_2$	**3d** + **5a**	$Zn(OAc)_2$, quinoline, 210 °C	70	amorphous
6	**6d**	N	O	$CH(C_6H_{13})_2$	**3f** + **5a**	$Zn(OAc)_2$, quinoline, 210 °C	72	predominantly amorphous
7	**6e**	N	S	$CH(C_6H_{13})_2$	–[b]	$Pd(dba)_2$, (2-furyl)$_3$P, THF	68	predominantly amorphous
8	**7a**	–	O	$CH(C_6H_{13})_2$	**4b** + **5a**	$Zn(OAc)_2$, quinoline, 210 °C	80	amorphous
9	**10a**	–	O	$CH(C_6H_{13})_2$	**4b** + **8a**	quinoline, microwaves	75	crystalline
10	**8a**	–	–	$CH(C_6H_{13})_2$				–
11	**9a**	CH	S	$CH(C_6H_{13})_2$	–[c]	$Pd(dba)_2$, (2-furyl)$_3$P, THF	42	crystalline
12	**9b**	CH	O	$CH(C_6H_{13})_2$	**3d** + **8a**	quinoline, microwaves	74	amorphous
13	**9c**	N	S	$CH(C_6H_{13})_2$	**3e** + **8a**	quinoline, 210 °C	75	amorphous
14	**9d**	N	O	$CH(C_6H_{13})_2$	**3f** + **8a**	quinoline, microwaves	77	amorphous

[a] From 2-(1-hexylheptyl)-9-(4-iodophenyl)anthra[2,1,9-*def*:6,5,10-*d*′*e*′*f*′]diisoquinoline-1,3,8,10-tetraone with **2a**.
[b] From 2-(1-hexylheptyl)-9-(5-iodopyridin-2-yl)anthra[2,1,9-*def*:6,5,10-*d*′*e*′*f*′]diisoquinoline-1,3,8,10-tetraone with **2a**.
[c] From 6-(4-iodophenyl)-2,10-bis(1-hexylheptyl)-1*H*-pyrrolo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d*′*e*′*f*′]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone with **2a**.



Scheme 3

(Scheme 4). The zinc organometallic derivative of **3** was prepared from the iodo compound **3h** by means of zinc chloride and magnesium, however proved to be less reactive than **2a** in the cross-coupling with **11**; better results were obtained with the iodo compound **13** to form **14** (Scheme 4). Finally, a benzothiadiazole was directly attached to perylenetetracarboxylic bisimide by the condensation of **5** with 4,7-dibromo-2,1,3-benzothiadiazol-5-amine to form the crystalline **15** (for the structure, see the experimental section).

The UV/Vis spectra of the heterocyclically extended perylene derivatives are dominated by the strong, structured, bathochromic absorption of the perylenecarboxylic imide chromophores. The absorption of **6a** compared with the purely aliphatically substituted reference compound *N*,*N*′-bis(1-hexylheptyl)-3,4:9,10-perylenebis(dicarboximide) (**S-13**) exhibits an additional weaker absorption between 290 and 380 nm caused by the attached 2,1,3-benzothiadiazole; see Figure 1. Interestingly the additional absorption matches the emission of the mercury line at 365 nm as a very intense UV light source. The fluorescence of the attached heterocycle in **6a** is completely suppressed and only the strong, bathochromic emission of the perylene unit was found indicating an efficient energy transfer by FRET. The fluorescence quantum yield of **6a** and **6b**, respectively, are close to 100% both for the irradiation of the perylene chromophore and for the 2,1,3-benzothiadiazole unit, indicating the domination of the Förster-type energy transfer[11] (FRET) over alternative processes for deactivation.

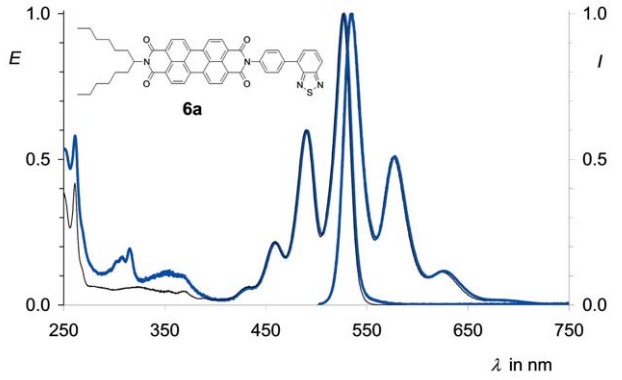


Figure 1 UV/Vis absorption and fluorescence spectra ($CHCl_3$); *thin line*: Standard perylene dye **S-13**; *thick line, left*: Absorption of **6a**; *thick line, right*: fluorescence spectra of **6a**; the spectra of **6b** are congruent to those of **6a**.

The most bathochromic absorption of **9a** is found at shorter wavelengths than for **6a**; additional absorption bands were found caused by the attached heterocycle such as in **6a** (Figure 2). The fluorescence of the basic perylene chromophore in **9a** was efficiently quenched. This is interpreted in terms of a photo-induced electron transfer (PET) from the electron-rich 2,1,3-benzothiadiazole to the comparably electron-deficient, electronically excited benzoperylene chromophore; compare with the literature.[12]

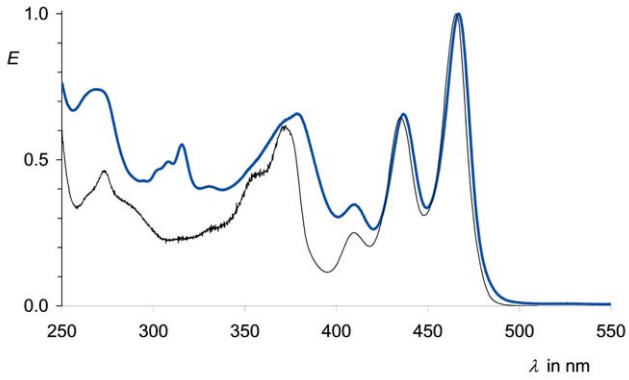
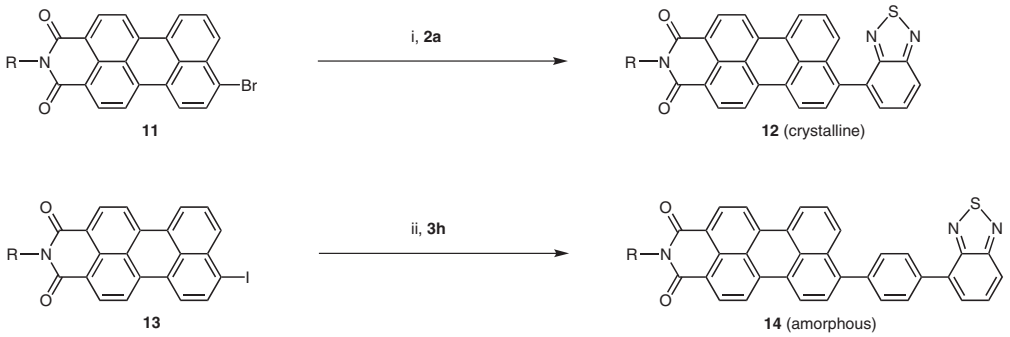


Figure 2 *Thick line*: UV/Vis absorption spectrum of **9a** ($CHCl_3$); *thin line*: UV/Vis absorption spectrum of 6-cyclohexyl-2,10-bis(1-hexylheptyl)-1*H*-pyrrolo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d*′*e*′*f*′]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone as a typical example for benzoperylenehexacarboxylic trisimides.

The UV/Vis spectra of **12** are slightly bathochromically shifted in the visible compared with standard perylene-3,4-dicarboximides; the typical double maximum structure is preserved; see Figure 3. There is an additional absorption of the heterocyclic side chain at about 300 nm. The fluorescence spectrum is broad, slightly structured



Scheme 4 Synthesis of 2,1,3-benzothiadiazoloperylenes. *Reagents and conditions*: (i) $Pd(OAc)_2$, SPhos (4 mol%), THF, 20 °C, 24 h; (ii) 1. **3h**, LiCl, Mg, $ZnCl_2$, THF; 2. **13**, $Pd(dba)_2$, $(furyl)_3P$.

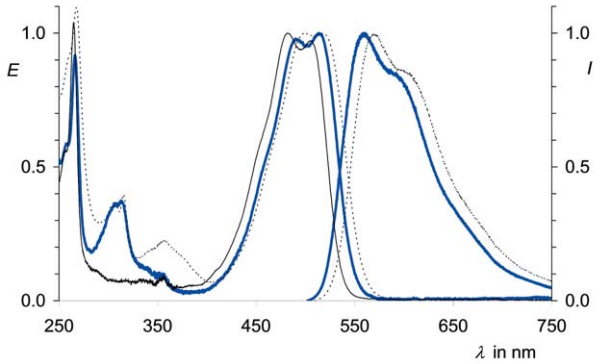


Figure 3 UV/Vis absorption and fluorescence spectra ($CHCl_3$); *thin line*: 2-(1-Hexylheptyl)-1*H*-perylo[3,4-*cd*]pyridine-1,3(2*H*)-dione as typical example for perylene-3,4-dicarboxylic imides; *thick line, left*: Absorption of **12**, *dotted line*: **14**; *thick line, right*: Fluorescence spectra of **12** (*thick line*) and **14** (*dotted line*).

and extends to the near infrared (NIR). The fluorescence is strong where a fluorescence quantum yield of 90% was obtained in chloroform. The introduction of a phenyl spacer in **14** causes a further slight bathochromic shift both for the UV/Vis absorption and fluorescence where the structuring of the spectra is similar to **12**, however less pronounced. The fluorescence quantum yield of **14** increased by the introduction of the phenyl spacer to close to 100%.

The bichromophoric **6a** dissolved in dichloromethane and precipitated with methanol is obtained as an amorphous, voluminous red precipitate without any tendency for crystallization and resembles precipitated aluminum hydroxide, except for the red color. The XRD spectrum indicates an amorphous structure up to microscopic dimensions since no sharp reflexes were obtained (Figure 4). A prolongation of the side chain in **6b** lowers the molecular interactions further and preserves the amorphous structure; see Figure 5. Precipitation with methanol forms a red liquid phase with the impression of homogeneity being able to pass standard D4 glass filters.

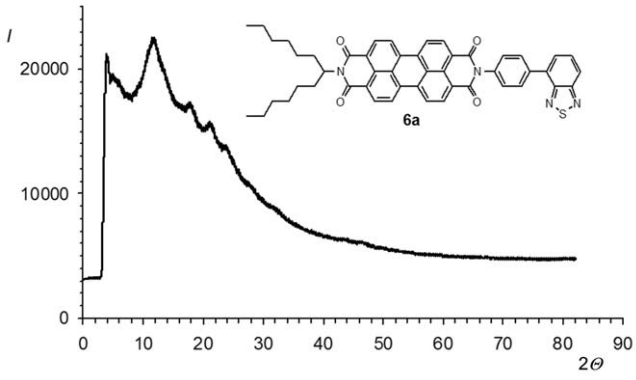


Figure 4 XRD spectrum of **6a** (MoKα)

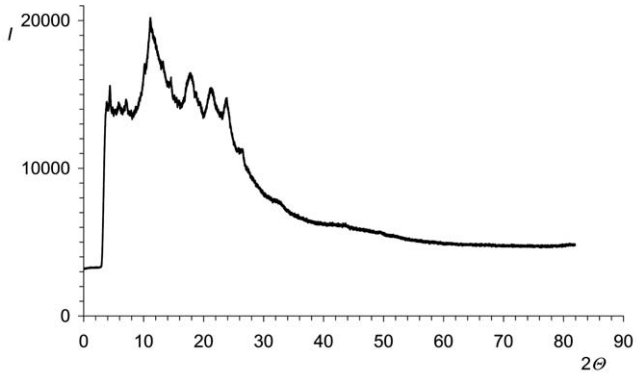


Figure 5 XRD spectrum of **6b** (MoKα)

DLS measurement of this phase indicates the formation of nanoparticles with a particle size of 28 nm; (Figure 6). A REM micrograph of the evaporated solution verifies such a nano structure (Figure 7). Obviously, the prolongation of the swallow-tail alkyl side chain diminishes the molecular interactions so far that no amorphous macroscopic aggregates are formed such as for **6a**, but the continuation of aggregation stops at nanometer dimensions. Compound **6e** with the more polar pyridyl spacer seems to be slightly more ordered. The disordering effect of 2,1,3-benzothiadiazole seems to be more general because it was also found for compounds **9**, **10**, **12**, and **14**, however, not as pronounced as for **6** where no tendency for the formation of ordered arrangements could be detected for **6a** and **6b**, respectively; see Figure 8 and compare with Figure 4.

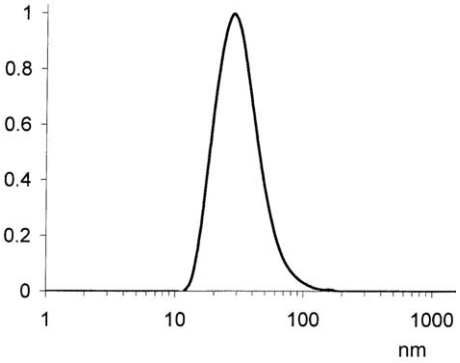


Figure 6 DLS measurement of **6b** precipitated with methanol from dichloromethane

In summary, 2,1,3-benzothiadiazole and 2,1,3-benzoxadiazole moieties could be efficiently attached to perylene- and benzoperylenecarboxylic imides by using a palladium-catalyzed cross-coupling with the new zincated 2,1,3-benzothiadiazoles **2a** and 2,1,3-benzoxadiazoles **2b**. Such dyads were obtained as amorphous macroscopic (**6a**) and amorphous nanomaterials (**6b**), respectively. The perylene derivatives **6** exhibit FRET-type energy transfer with efficiencies close to 100% and the similar benzoperylene derivatives **9** highly efficient photoinduced charge separation by electron transfer (PET), respectively. The

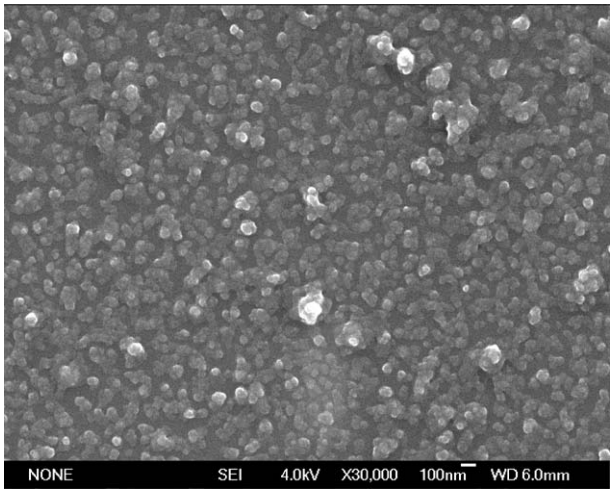


Figure 7 REM micrograph of **6b** precipitated with methanol from dichloromethane and then evaporated

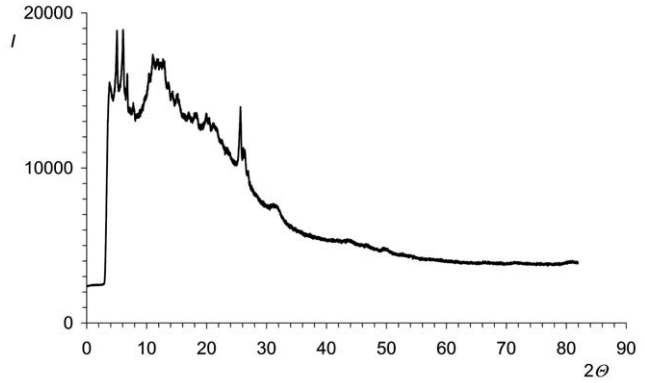


Figure 8 XRD spectrum of **12** (MoKα)

combination of these photophysical effects and the amorphous structures make such materials especially interesting for photovoltaic and OLED applications because they avoid interfering grain boundaries of microcrystallinity. One may expect that 2,1,3-benzothiadiazole and 2,1,3-benzoxadiazole moieties are more generally useful for the generation of amorphous structures when combined with chromophores.

The reactions were carried out under an argon atmosphere in flame-dried glassware if indicated. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under N_2. Column chromatography was performed using silica gel (0.040–0.063 mm, 230–400 mesh ASTM) from Merck. IR spectra: Perkin Elmer 1420 Ratio Recording Infrared Spectrophotometer, FT 1000 and Perkin Elmer BXII FT-IR with ATR-unit; UV/Vis spectra: Varian Cary 5000 and Bruins Omega 20; fluorescence spectra: Varian Cary Eclispe; NMR spectroscopy: Varian Vnmrs 600 (600 MHz); mass spectroscopy: Finnigan MAT 95. References for the fluorescence quantum yield: **A** = *N*,*N*′-Bis(1-hexylheptyl)-3,4:9,10-perylenebis(dicarboximide) (**S-13**)[13] (RN 110590-84-6); **B** = perylene-3,4,9,10-tetramethyl ester (RN 53159-49-2); **C** = 2,10-bis(1-hexylheptyl)-6-{2-[3,8,9,10-tetrahydro-9-(1-octylnonyl)-1,3,8,10-tetraoxoanthra[2,1,9-*def*:6,5,10-*d*′*e*′*f*′]diisoquinolin-2(1*H*)-yl]ethyl}-1*H*-pyrrolo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d*′*e*′*f*′]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone (**C25**)[14] (RN 335458-21-4). 2-Dicyclohexyl(2′,6′-dimethoxybiphenyl)phosphine = SPhos. For NMR assignments, H_{bper} and H_{per} are used to indicate protons on the benzoperylene and perylene moieties, respectively.

2,1,3-Benzothiadiazol-4-ylzinc Chloride (2a)
A 0.6 M soln of $TMP_2Mg{\cdot}2LiCl$ in THF (23.0 mL) was added in a dry Schlenk tube under an argon atmosphere dropwise to a soln of 2,1,3-benzothiadiazole (**1a**; 1.4 g, 10 mmol) in anhyd THF (10 mL) at –40 °C. The mixture was stirred for 14 h at this temperature and then treated dropwise with 1.0 M $ZnCl_2$ in anhyd THF (15 mL) and stirred at –40 °C for 30 min. The mixture was allowed to warm to 20 °C to give the zinc reagent **2a**; yield: ca. 85%.

2,1,3-Benzoxadiazol-4-ylzinc Chloride (2b)
A 1.2 M soln of TMPMgCl·LiCl in anhyd THF (1.7 mL) was added in a dry Schlenk tube under an argon atmosphere dropwise to a soln of 2,1,3-benzoxadiazole (**1b**; 220 mg, 1.8 mmol) in anhyd THF (2 mL) at –5 °C. The mixture was stirred for 14 h at this temperature and then treated dropwise with 1.0 M $ZnCl_2$ in anhyd THF (2.1 mL) and stirred at –5 °C for 30 min. The mixture was allowed to warm up to 20 °C to provide the zinc reagent **2b**; yield: ca. 80%.

4-(2,1,3-Benzothiadiazol-4-yl)aniline (3c); Typical Procedure
Under argon, 0.25 M soln of **2a** in anhyd THF (3 mmol), $Pd(OAc)_2$ (14 mg, 0.06 mmol), SPhos (49 mg, 0.12 mmol), and 4-iodoaniline (855 mg, 3.9 mmol) were stirred at 50 °C for 24 h. The reaction was quenched by the addition of sat. aq NH_4Cl soln (15 mL) and extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were dried ($MgSO_4$), evaporated in vacuo, and purified by column chromatography (silica gel, CH_2Cl_2) to give **3c** as a brown solid; yield: 415 mg (61%); mp 131.6–133.2 °C.

IR (ATR): 1627 (m), 1608 (m), 1512 (s), 1297 (m), 1181 (m), 1124 (m), 827 (m), 802 (s), 753 cm^{-1} (vs).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.94–7.88 (m, 1 H), 7.76–7.67 (m, 4 H), 6.72–6.68 (m, 2 H), 5.40 (br s, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 155.3, 152.8, 149.2, 134.0, 130.3, 129.9, 125.4, 123.9, 118.3, 113.6.

MS (70 eV, EI): *m*/*z* (%) = 229 (5), 228 (15), 227 (100) [M^+], 226 (15), 211 (5), 194 (5), 181 (4), 168 (3), 140 (4), 114 (5).

HRMS (EI): *m*/*z* [$M]^+$ calcd for $C_{12}H_9N_3S$: 227.0517; found: 227.0517.

3-(2,1,3-Benzothiadiazol-4-yl)aniline (4a)
Following the typical procedure for **3c** using 0.25 M **2a** in anhyd THF (3 mmol), $Pd(OAc)_2$ (14 mg, 0.06 mmol), SPhos (49 mg, 0.12 mmol), 3-iodoaniline (855 mg, 3.9 mmol), and sat. aq NH_4Cl soln (15 mL) with purification by column chromatography (silica gel, pentane–EtOAc, 3:1) gave **4a** as an ochre solid; yield: 414 mg (61%); mp 93.2–94.6 °C.

IR (ATR): 3435 (m), 3346 (m), 1623 (m), 1582 (m), 1478 (m), 1165 (m), 850 (m), 778 (s), 760 (s), 698 cm^{-1} (s).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.03 (dd, *J* = 8.6, 1.4 Hz, 1 H), 7.78–7.71 (m, 2 H), 7.18–7.14 (m, 2 H), 7.05–7.03 (m, 1 H), 6.67–6.64 (m, 1 H), 5.20 (br s, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 155.1, 152.8, 148.7, 137.5, 134.4, 130.1, 128.9, 127.5, 119.9, 116.8, 114.6, 114.0.

MS (70 eV, EI): *m*/*z* (%) = 229 (4), 228 (11), 227 (100) [M^+], 226 (14), 211 (5), 200 (3), 199 (3), 194 (2), 181 (3), 140 (3), 114 (3).

HRMS (EI): *m*/*z* [$M]^+$ calcd for $C_{12}H_9N_3S$: 227.0517; found: 227.0503.

5-(2,1,3-Benzothiadiazol-4-yl)pyridin-2-amine (3e)
Following the typical procedure for **3c** using 0.25 M **2a** in anhyd THF (3 mmol), $Pd(OAc)_2$ (14 mg, 0.06 mmol), SPhos (49 mg,

0.12 mmol), 5-iodopyridin-2-amine (885 mg, 3.9 mmol), and sat. aq NH_4Cl soln (15 mL) with purification by column chromatography (silica gel, EtOAc) gave **3e** as a yellow solid; yield: 360 mg (53%); mp 194.9–196.6 °C.

IR (ATR): 1640 (s), 1628 (s), 1594 (m), 1506 (m), 1482 (s), 1382 (m), 1272 (m), 827 (m), 805 (s), 755 cm^{-1} (vs).

^1H NMR (400 MHz, DMSO-d_6): δ = 8.60 (dd, J = 2.5, 0.7 Hz, 1 H), 8.03 (dd, J = 8.6, 2.5 Hz, 1 H), 7.98–7.93 (m, 1 H), 7.75–7.70 (m, 2 H), 6.59 (dd, J = 8.7, 0.7 Hz, 1 H), 6.25 (br s, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 159.6, 155.1, 152.6, 148.2, 137.4, 131.4, 130.3, 125.5, 120.7, 119.0, 107.5.

MS (70 eV, EI): m/z (%) = 229 (11), 228 (100) [M^+], 227 (21), 201 (11), 200 (7), 69 (8), 57 (10), 55 (10), 43 (8), 41 (6).

HRMS (EI): m/z [$M]^+$ calcd for $C_{11}H_8N_4S$: 228.0470; found: 228.0461.

4-[4-(Trimethylsilyl)phenyl]-2,1,3-benzothiadiazole (3g)
Following the typical procedure for **3c** using 0.25 M **2a** in anhyd THF (3 mmol), $Pd(dba)_2$ (25 mg, 0.06 mmol), $(furyl)_3P$ (mg, 0.12 mmol), (4-bromophenyl)trimethylsilane (1.03 g, 4.5 mmol), and sat. aq NH_4Cl soln (10 mL) with purification by column chromatography (silica gel, pentane) gave **3g** as a light-yellow solid; yield: 355 mg (42%); mp 120.6–122.4 °C.

IR (ATR): 3058 (w), 1946 (w), 1595 (w), 1474 (w), 1412 (w), 1168 (w), 850 (m), 825 (m), 799 (vs), 751 (s), 713 cm^{-1} (w).

^1H NMR (300 MHz, $CDCl_3$): δ = 8.01–7.97 (m, 1 H), 7.91–7.88 (m, 2 H), 7.71–7.66 (m, 4 H), 0.32 (s, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.6, 153.6, 140.9, 137.7, 134.7, 133.6, 129.6, 128.5, 127.7, 120.6, –1.1.

MS (70 eV, EI): m/z (%) = 286 (3), 285 (5), 284 (22) [M^+], 272 (2), 271 (9), 270 (19), 269 (100), 253 (2), 239 (6), 135 (4).

HRMS (EI): m/z [$M]^+$ calcd for $C_{15}H_{16}N_2SSi$: 284.0803; found: 284.0799.

4-(4-Iodophenyl)-2,1,3-benzothiadiazole (3h)
ICl (2 mL) was added to thiadiazole **3g** (284 mg, 1 mmol) in CH_2Cl_2 (2 mL) and the mixture was stirred at 0 °C for 3 h. The reaction was quenched by the addition of sat. aq $Na_2S_2O_3$ soln (10 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were dried ($MgSO_4$), evaporated in vacuo, and purified by column chromatography (silica gel, pentane–Et_2O, 200:1) to give **3h** as a light-yellow solid; yield: 316 mg (93%); mp 71.2–72.9 °C.

IR (ATR): 3063 (w), 1594 (w), 1249 (m), 1130 (w), 1096 (w), 895 (w), 840 (s), 823 (s), 803 (s), 756 (vs), 678 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 8.06–8.00 (m, 1 H), 7.90–7.85 (m, 2 H), 7.72–7.67 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.6, 153.2, 137.8, 136.8, 133.4, 131.0, 129.6, 127.6, 121.0, 94.5.

MS (70 eV, EI): m/z (%) = 339 (15), 338 (100), 212 (10), 211 (57), 178 (15), 165 (7), 152 (9), 140 (12), 58 (11), 43 (39).

HRMS (EI): m/z [$M]^+$ calcd for $C_{12}H_7IN_2S$: 337.9375; found: 337.9370.

4-(2,1,3-Benzoxadiazol-4-yl)aniline (3d); Typical Procedure
Under argon, 0.25 M **2b** in anhyd THF (1.4 mmol), $Pd(OAc)_2$ (7 mg, 0.03 mmol), SPhos (25 mg, 0.06 mmol), and 4-iodoaniline (375 mg, 1.7 mmol) were stirred at 50 °C for 24 h. The reaction was quenched by the addition of sat. aq NH_4Cl soln (10 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were dried ($MgSO_4$), evaporated in vacuo, and purified by column chromatography (silica gel, pentane–EtOAc, 4:1) to give **3d** as a brown solid; yield: 175 mg (59%); mp 115.4–116.6 °C.

IR (ATR): 3453 (w), 3364 (m), 3217 (w), 1626 (m), 1603 (s), 1544 (w), 1510 (s), 1447 (w), 1423 (w), 1373 (w), 1302 (m), 1276 (m), 1178 (w), 1141 (w), 1016 (w), 892 (w), 871 (w), 836 (m), 815 (m), 797 (s), 754 cm^{-1} (vs).

^1H NMR (400 MHz, DMSO-d_6): δ = 7.82–7.79 (m, 3 H), 7.65–7.56 (m, 2 H), 6.72–6.69 (m, 2 H), 5.58 (br s, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 150.1, 149.7, 148.2, 133.2, 129.3, 129.1, 125.3, 121.6, 113.8, 112.1.

MS (70 eV, EI): m/z (%) = 212 (13), 211 (100) [M^+], 210 (7), 194 (8), 182 (10), 181 (53), 179 (7), 155 (11), 154 (10), 153 (9), 127 (10).

HRMS (EI): m/z [$M]^+$ calcd for $C_{12}H_9N_3O$: 211.0746; found: 211.0741.

3-(2,1,3-Benzoxadiazol-4-yl)aniline (4b)
Following the typical procedure for **3d** using 0.2 M **2b** in anhyd THF (1.4 mmol), $Pd(OAc)_2$ (7 mg, 0.03 mmol), SPhos (25 mg, 0.06 mmol), and 3-iodoaniline (375 mg, 1.7 mmol) with purification by column chromatography (silica gel, pentane–EtOAc, 2:1) gave **4b** as a yellow solid; yield 160 mg (55%); mp 95.8–97.4 °C.

IR (ATR): 3400 (w), 1602 (m), 1583 (m), 1311 (w), 1018 (w), 889 (w), 870 (m), 859 (m), 784 (s), 746 (vs), 694 cm^{-1} (s).

^1H NMR (400 MHz, DMSO-d_6): δ = 9.96 (dd, J = 8.8, 1.0 Hz, 1 H), 7.71–7.64 (m, 2 H), 7.23–7.16 (m, 2 H), 7.12–7.09 (m, 1 H), 6.70–6.67 (m, 1 H), 5.30 (br s, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 149.6, 149.1, 148.2, 135.4, 133.0, 129.7, 129.4, 128.5, 115.6, 114.8, 114.4, 113.4.

MS (70 eV, EI): m/z (%) = 212 (10), 211 (76) [M^+], 182 (16), 181 (100), 179 (9), 168 (11), 154 (17), 153 (8), 149 (8), 127 (12).

HRMS (EI): m/z [$M]^+$ calcd for $C_{12}H_9N_3O$: 211.0746; found: 211.0737.

5-(2,1,3-Benzoxadiazol-4-yl)pyridin-2-amine (3f)
Following the typical procedure for **3d** using 0.25 M **2b** in anhyd THF (1.4 mmol), $Pd(OAc)_2$ (7 mg, 0.03 mmol), SPhos (25 mg, 0.06 mmol), and 5-iodopyridin-2-amine (375 mg, 1.7 mmol) with purification by column chromatography (silica gel, EtOAc) gave **3f** as an orange solid; yield: 160 mg (54%); mp 166.9–168.8 °C.

IR (ATR): 3414 (m), 3322 (w), 3118 (m), 1653 (s), 1612 (m), 1600 (s), 1545 (w), 1505 (vs), 1395 (s), 1372 (m), 1334 (w), 1322 (m), 1298 (m), 1269 (m), 1139 (m), 1081 (w), 1011 (w), 889 (w), 872 (w), 815 (w), 797 (m), 759 (w), 744 (s), 713 (w), 661 cm^{-1} (w).

^1H NMR (400 MHz, DMSO-d_6): δ = 8.69–8.68 (m, 2 H), 8.06 (dd, J = 8.7, 2.6 Hz, 1 H), 7.87 (dd, J = 8.9, 0.7 Hz, 1 H), 7.71 (dd, J = 6.9, 0.8 Hz, 1 H), 7.62 (dd, J = 8.9, 6.9 Hz, 1 H), 6.60 (dd, J = 8.7, 0.7 Hz, 1 H), 6.41 (br s, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 160.1, 149.6, 148.0, 147.9, 136.3, 133.2, 126.8, 125.9, 118.6, 113.0, 107.9.

MS (70 eV, EI): m/z (%) = 213 (15), 212 (100) [M^+], 196 (9), 185 (8), 182 (11), 155 (17), 142 (8), 128 (8), 57 (8).

HRMS (EI): m/z [$M]^+$ calcd for $C_{11}H_8N_4O$: 212.0698; found: 212.0690.

4-Phenyl-2,1,3-benzoxadiazole (3b)
A 0.25 M soln of **2b** in anhyd THF (1.4 mmol) under argon, $Pd(OAc)_2$ (7 mg, 0.03 mmol), $(furyl)_3P$ (25 mg, 0.06 mmol), and iodobenzene (347 mg, 1.7 mmol) were stirred at 25 °C for 6 h. The reaction was quenched with sat. aq NH_4Cl soln (10 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were dried ($MgSO_4$), evaporated in vacuo, and purified by column chromatography (silica gel, pentane) to give **3b** as a light-brownish solid; yield: 244 mg (69%); mp 64.5–65.3 °C; R_f = 0.8 (toluene).

IR (ATR): 3082 (w), 1582 (s), 1494 (m), 1016 (m), 828 (m), 803 (m), 761 (s), 750 (s), 697 (s), 679 cm^{-1} (m).

^1H NMR (600 MHz, $CDCl_3$, 27.0 °C, TMS): δ = 7.99–7.97 (m, 2 H, H_{Ph}), 7.79 (dd, $^3J_{H,H}$ = 8.9 Hz, $^4J_{H,H}$ = 0.8 Hz, 1 H, H_{arom}), 7.57 (dd,

$^3J_{H,H}$ = 6.8 Hz, $^4J_{H,H}$ = 0.8 Hz, 1 H, H_{arom}), 7.54–7.51 (m, 2 H, H_{Ph}), 7.49 (dd, $^3J_{H,H}$ = 6.8 Hz, $^3J_{H,H}$ = 8.9 Hz, 1 H, H_{arom}), 7.47–7.44 (m, 1 H, H_{Ph}).

^{13}C NMR (150 MHz, $CDCl_3$, 27 °C): δ = 149.8, 148.6, 135.3, 131.8, 130.5, 129.3, 128.9, 128.4, 128.0, 115.0.

MS (70 eV, EI): *m*/*z* (%) = 196 (88) [M^+], 166 (100) [M^+ – NO].

HRMS: *m*/*z* [M]$^+$ calcd for $C_{12}H_8N_2O$: 196.0637; found: 196.0631.

Anal. Calcd for $C_{12}H_8N_2O$ (196.1): C, 73.46; H, 4.11; N, 14.28. Found: C, 73.35; H, 4.12; N, 14.04.

8-(2,1,3-Benzothiadiazol-4-yl)-2-(1-hexylheptyl)-1*H*-perylo[3,4-*cd*]pyridine-1,3(2*H*)-dione (12)

Under an argon atmosphere, 0.3 M **2a** in anhyd THF (0.85 mmol), $Pd(OAc)_2$ (5 mg, 0.02 mmol), SPhos (16 mg, 0.04 mmol), and 8-bromo-2-(1-hexylheptyl)-1*H*-perylo[3,4-*cd*]pyridine-1,3(2*H*)-dione (**11**; 63 mg, 0.13 mmol) were stirred at 20 °C for 24 h. The reaction was quenched by the addition of sat. aq NH_4Cl soln (5 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were dried ($MgSO_4$), evaporated in vacuo, dissolved in a small amount of CH_2Cl_2, and purified by column chromatography (silica gel, CH_2Cl_2, fraction with bright red color). The product dissolved in CH_2Cl_2 was precipitated with MeOH and collected by vacuum filtration to give **12** as a red solid; yield: 39 mg (47%); mp 184.4–184.7 °C; R_f = 0.56 (CH_2Cl_2).

IR (ATR): 3050 (w), 2924 (s), 1688 (s), 1650 (s), 1592 (s), 1456 (m), 1352 (s), 854 (m), 808 (s), 752 cm^{-1} (s).

^{1}H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 8.59–8.47 (m, 3 H, H_{per}), 8.39 (m, 3 H, H_{arom}), 8.17 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 1.2 Hz, 1 H, H_{arom}), 7.84–7.80 (m, 1 H, H_{arom}), 7.77–7.72 (m, 2 H, H_{arom}), 7.63 (d, $^3J_{H,H}$ = 8.4 Hz, 1 H, H_{arom}), 7.47 (m, 1 H, H_{arom}), 5.24–5.17 (m, 1 H, CH), 2.31–2.22 (m, 2 H, β-CH_2), 1.91–1.83 (m, 2 H, β-CH_2), 1.40–1.20 (m, 16 H, 8 CH_2), 0.83 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, 2 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27 °C): δ = 165.1, 164.1, 155.1, 154.3, 138.1, 136.8, 136.5, 133.2, 132.8, 132.0, 131.1, 130.3, 129.8, 129.7, 129.5, 129.4, 129.1, 128.8, 128.3, 127.0, 126.5, 123.7, 123.0, 121.6, 120.4, 120.3, 54.4, 32.4, 31.8, 29.3, 27.0, 22.6, 14.1.

MS (DEP/EI): *m*/*z* (%) = 637 (42) [M^+], 455 (100) [$M^+ – C_{13}H_{26}$].

HRMS: *m*/*z* [M]$^+$ calcd for $C_{41}H_{39}N_3O_2S$: 637.2763; found: 637.2751.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 314.0 (15600), 489.5 (37500), 513.3 nm (38400).

Fluorescence ($CHCl_3$): λ_{max} = 557.3 nm.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm,\ 1\ cm}$ = 0.0195, reference: **A** with Φ = 1.00): 0.90.

Anal. Calcd for $C_{41}H_{39}N_3O_2S$ (637.3): C, 77.21; H, 6.16; N, 6.59; S, 5.03. Found: C, 76.84; H, 6.30; N, 6.49; S, 5.12.

2-[4-(2,1,3-Benzothiadiazol-4-yl)phenyl]-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (6a); Typical Procedure

Under an argon atmosphere, 0.3 M **2a** in anhyd THF (0.85 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), (2-furyl)$_3$P (9 mg, 0.04 mmol), and 2-(1-hexylheptyl)-9-(4-iodophenyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone[13] (100 mg, 129 μmol) were stirred at 21 °C for 24 h. The reaction was quenched by the addition of sat. aq NH_4Cl soln (5 mL) and extracted with CH_2Cl_2 (3 × 30 mL), dried ($MgSO_4$), evaporated in vacuo, dissolved in a small amount of CH_2Cl_2, and purified by column chromatography (silica gel, CH_2Cl_2, fraction with bright-red color). The product dissolved in CH_2Cl_2 was precipitated with MeOH and collected by vacuum filtration to give **6a** as an amorphous red material; yield: 47 mg (60%); mp >300 °C; R_f = 0.1 (silica gel, CH_2Cl_2).

IR (ATR): 3476 (w), 2926 (m), 1696 (s), 1660 (s), 1594 (s), 1352 (s), 1254 (s), 864 (m), 810 (s), 793 (m), 746 cm^{-1} (m).

^{1}H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 8.74–8.64 (m, 8 H, H_{per}), 8.18 (d, $^3J_{H,H}$ = 8.3 Hz, 2 H, H_{arom}), 8.05 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, H_{arom}), 7.81 (d, $^3J_{H,H}$ = 7.1 Hz, 1 H, H_{arom}), 7.73 (dd, $^3J_{H,H}$ = 7.2 Hz, $^3J_{H,H}$ = 8.5 Hz, 1 H, H_{arom}), 7.53 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, H_{arom}), 5.23–5.16 (m, 1 H, CH), 2.29–2.23 (m, 2 H, β-CH_2), 1.92–1.83 (m, 2 H, β-CH_2), 1.39–1.19 (m, 16 H, 8 CH_2), 0.83 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, 2 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27 °C): δ = 163.6, 155.6, 153.4, 137.9, 135.3, 135.1, 134.4, 133.6, 132.0, 130.3, 129.6, 128.8, 128.1, 126.8, 126.5, 123.4, 123.3, 123.1, 121.0, 54.8, 32.4, 31.8, 29.7, 29.2, 26.9, 22.6, 14.0.

MS (DEP/EI): *m*/*z* (%) = 783 (36) [M^+ + H], 600 (100) [$M^+ – C_{13}H_{26}$].

HRMS: *m*/*z* [M]$^+$ calcd for $C_{49}H_{42}N_4O_4S$: 782.2927; found: 782.2845.

UV/Vis ($CHCl_3$): λ_{max} (ε)= 315.9 (17400), 352.0 (10500), 459.1 (19100), 491.0 (52700), 527.4 nm (87900).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 534.2 (1.00), 576.8 (0.51), 625.1 nm (0.12).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm,\ 1\ cm}$ = 0.1303, reference: **A** with Φ = 1.00): 1.00.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 353 nm, $E_{353\ nm,\ 1\ cm}$ = 0.0026, reference: **C** with Φ = 1.00): 1.00.

Anal. Calcd for $C_{49}H_{42}N_4O_4S$ (782.3): C, 75.17; H, 5.41; N, 7.16; S, 4.10. Found: C, 75.27; H, 5.48; N, 6.81; S, 4.02.

2-[4-(2,1,3-Benzothiadiazol-4-yl)pyridin-2-yl]-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone (6e)

Following the typical procedure for **6a** using 0.3 M **2a** in anhyd THF (0.85 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), (2-furyl)$_3$P (9 mg, 0.04 mmol) and 2-(1-hexylheptyl)-9-(5-iodopyridin-2-yl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10-tetraone[13] (150 mg, 191 μmol) and sat. aq NH_4Cl soln (5 mL) with and purification by column chromatography (fine silica gel, CH_2Cl_2–MeOH, 60:1, 1st main fraction with bright-red color). The product dissolved in a small amount of CH_2Cl_2 was precipitated with MeOH, collected by vacuum filtration, and dried in vacuo to give **6e** as a predominantly amorphous red material; yield: 103 mg (68%); mp > 300 °C; R_f = 0.45 (CH_2Cl_2–MeOH, 60:1).

IR (ATR): 3342 (w), 3067 (w), 2922 (m), 1696 (s), 1654 (s), 1592 (s), 1576 (s), 1338 (s), 1252 (s), 810 (s), 745 cm^{-1} (s).

^{1}H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 9.26 (s, 1 H, H_{arom}), 8.70–8.57 (m, 9 H, H_{per}, H_{arom}), 8.10 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, H_{arom}), 7.86 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, H_{arom}), 7.77 (dd, $^3J_{H,H}$ = 8.8 Hz, $^3J_{H,H}$ = 6.9 Hz, 1 H, H_{arom}), 7.64 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, H_{arom}), 5.22–5.17 (m, 1 H, CH), 2.29–2.22 (m, 2 H, β-CH_2), 1.92–1.86 (m, 2 H, β-CH_2), 1.38–1.20 (m, 16 H, 8 CH_2), 0.83 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, 2 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27 °C): δ = 164.5, 163.4, 155.2, 153.1, 149.8, 148.8, 139.3, 135.2, 134.1, 133.6, 131.7, 130.1, 129.8, 129.5, 128.3, 126.6, 126.3, 123.8, 123.1, 123.0, 121.9, 54.8, 32.4, 31.7, 29.2, 27.0, 22.6, 14.0.

MS (DEP/EI): *m*/*z* (%) = 784 (22) [M^+ + H], 601 (100) [$M^+ – C_{13}H_{26}$].

HRMS: *m*/*z* [M]$^+$ calcd for $C_{48}H_{41}N_5O_4S$: 783.2879; found: 783.2876.

UV/Vis ($CHCl_3$): λ_{max} (ε)= 315.0 (15400), 349.3 (8600), 459.6 (19800), 491.0 (54800), 527.4 nm (91400).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 534.2 (1.00), 577.1 (0.51), 625.7 nm (0.12).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm,\ 1\ cm}$ = 0.0135, reference: **A** with Φ = 1.00): 1.00.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 353 nm, $E_{353\ nm,\ 1\ cm}$ = 0.0027, reference: **C** with Φ = 1.00): 0.98.

Anal. Calcd for $C_{48}H_{41}N_5O_4S$ (783.3): C, 73.54; H, 5.27; N, 8.93; S, 4.09; found: C, 73.33; H, 5.34; N, 8.90; S, 4.16.

6-[4-(2,1,3-Benzothiadiazol-4-yl)phenyl]-2,10-bis(1-hexylheptyl)-1*H*-pyrrolo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone (9a)

Following the typical procedure for **6a** using 0.3 M **2a** in anhyd THF (0.85 mmol), $Pd(dba)_2$ (12 mg, 0.02 mmol), (2-furyl)$_3$P (9 mg, 0.04 mmol), and 6-(4-iodophenyl)-2,10-bis(1-hexylheptyl)-1*H*-pyrrolo[3′,4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone (210 mg, 198 μmol), and sat. aq NH_4Cl soln (5 mL) to give **9a** as a yellow solid; yield: 88 mg (42%); mp > 300 °C; R_f = 0.21 ($CHCl_3$).

IR (ATR): 3074 (w), 2924 (s), 1710 (s), 1661 (s), 1364 (s), 1316 (s), 846 (m), 811 (s), 764 (s), 749 cm^{-1} (s).

^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 10.34–10.30 (m, 2 H, H_{bper}), 9.18–9.06 (m, 4 H, H_{bper}), 8.26 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, H_{arom}), 8.06 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 1.0 Hz, 1 H, H_{arom}), 7.97 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, H_{arom}), 7.87 (d, $^3J_{H,H}$ = 7.6 Hz, 1 H, H_{arom}), 7.76 (dd, $^3J_{H,H}$ = 6.8 Hz, $^3J_{H,H}$ = 8.8 Hz, 1 H, H_{arom}), 5.32–5.27 (m, 2 H, CH), 2.42–2.32 (m, 4 H, β-CH_2), 2.04–1.97 (m, 4 H, β-CH_2), 1.48–1.24 (m, 32 H, 8 CH_2), 0.83 (t, $^3J_{H,H}$ = 7.1 Hz, 12 H, 2 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27 °C, TMS): δ = 166.7, 164.4, 163.8, 163.3, 162.7, 155.6, 153.7, 137.2, 133.6, 131.4, 130.7, 130.1, 129.7, 128.9, 128.1, 127.4, 126.8, 126.7, 125.7, 125.0, 124.4, 123.7, 122.8, 121.0, 55.4, 32.4, 31.8, 29.3, 27.1, 22.6, 14.1.

MS (DEP/EI): *m*/*z* (%) = 1058 (9) [M^+ + H], 876 (37) [M^+ + H – $C_{13}H_{26}$], 694 (100) [M^+ + H –2 $C_{13}H_{26}$].

HRMS: *m*/*z* [M]$^+$ calcd for $C_{66}H_{67}N_5O_6S$: 1057.4812; found: 1057.4824.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 270.4 (44100), 315.9 (33600), 378.8 (38000), 409.4 (20600), 436.8 (39300), 466.8 nm (59400).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 436 nm, $E_{436\ nm,\ 1\ cm}$ = 0.0140, reference: **A** with Φ = 1.00): <0.01.

Anal. Calcd for $C_{66}H_{67}N_5O_6S$ (1057.5): C, 74.90; H, 6.38; N, 6.62; S, 3.03; found: C, 74.56; H, 6.26; N, 6.62; S, 3.14.

2-[4-(2,1,3-Benzoxadiazol-4-yl)phenyl]-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (6c); Typical Procedure

Under argon, 4-(2,1,3-benzoxadiazol-4-yl)aniline (**3d**; 42 mg, 0.20 mmol), tetraone **5a** (115 mg, 200 μmol), $Zn(OAc)_2$ (7.4 mg, 40 μmol), and quinoline (2.5 mL) were stirred at 210 °C for 5 h (deeply red mixture). The mixture was allowed to cool slightly, added dropwise with intense stirring to 2 M aq HCl (300 mL), stirred for 2 h, and allowed to stand for 16 h. The product was collected by vacuum filtration, washed with 2 M aq HCl (300 mL), hot distilled H_2O (300 mL), and a mixture of MeOH and distilled H_2O (300 mL, 1:1), and dried in vacuo at 90 °C for 2 d. The residue was dissolved in the minimal amount of CH_2Cl_2 and purified by column chromatography (short column with alumina, CH_2Cl_2 and a further column with silica gel, CH_2Cl_2, deeply red first fraction) to give **6c** as an amorphous red material; yield: 108 mg (70%); mp >300 °C; R_f = 0.2 (CH_2Cl_2).

IR (ATR): 2925 (m), 1694 (s), 1658 (s), 1593 (s), 1345 (s), 1252 (s), 1176 (s), 843 (m), 810 (s), 744 cm^{-1} (s).

^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 8.80–8.68 (m, 8 H, H_{per}), 8.24 (d, $^3J_{H,H}$ = 8.8 Hz, 2 H, H_{arom}), 7.87 (d, $^3J_{H,H}$ = 8.8 Hz, 1 H, H_{arom}), 7.69 (d, $^3J_{H,H}$ = 6.8 Hz, 1 H, H_{arom}), 7.59–7.53 (m, 3 H, H_{arom}), 5.23–5.17 (m, 1 H, CH), 2.30–2.22 (m, 2 H, β-CH_2), 1.92–1.84 (m, 2 H, β-CH_2), 1.40–1.18 (m, 16 H, 8 CH_2), 0.84 (t, $^3J_{H,H}$ = 6.8 Hz, 6 H, 2 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27.0 °C): δ = 163.5, 149.8, 148.4, 135.9, 135.7, 135.3, 131.9, 129.9, 129.4, 129.3, 129.1, 128.5, 126.7, 126.6, 123.1, 116.7, 115.5, 54.6, 32.3, 32.2, 31.6, 29.6, 29.2, 28.9, 26.9, 26.7, 26.6, 22.4, 13.9.

MS (DEP/EI): *m*/*z* (%) = 766 (37) [M^+], 584 (100) [M^+ – $C_{13}H_{26}$].

HRMS: *m*/*z* [M]$^+$ calcd for $C_{49}H_{42}N_4O_5$: 766.3157; found: 766.3155.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 345.5 (12600), 459.8 (19600), 491.0 (53600), 527.4 nm (89300).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 534.8 (1.00), 577.2 nm (0.51).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 490 nm, $E_{490\ nm,\ 1\ cm}$ = 0.0122, reference **A** with Φ = 1.00): 0.93.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 350 nm, $E_{350\ nm,\ 1\ cm}$ = 0.0032, reference: **C** with Φ = 1.00): 0.85.

Anal. Calcd for $C_{49}H_{42}N_4O_5$ (766:3): C, 76.74; H, 5.52; N, 7.31. Found: C, 76.33; H, 5.69; N, 7.21.

2-[5-(2,1,3-Benzoxadiazol-4-yl)pyridin-2-yl]-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (6d)

Following the typical procedure for **6c** using 5-(2,1,3-benzoxadiazol-4-yl)pyridin-2-amine (**3f**; 43 mg, 0.20 mmol), **5a** (115 mg, 200 μmol), $Zn(OAc)_2$ (7.4 mg, 40 μmol), and quinoline (2.5 mL) to give **6d** as a predominantly amorphous red material; yield: 110 mg (72%); mp >300 °C; R_f = 0.5 (CH_2Cl_2–MeOH, 60:1).

IR (ATR): 3091 (w), 2924 (m), 1697 (s), 1653 (s), 1577 (s), 1339 (s), 1253 (s), 848 (m), 797 (s), 742 cm^{-1} (s).

^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 9.29 (d, $^4J_{H,H}$ = 2.5 Hz, 1 H, H_{arom}), 8.75–8.64 (m, 9 H, H_{per}, H_{arom}), 7.94 (dd, $^3J_{H,H}$ = 9.0 Hz, $^4J_{H,H}$ = 0.6 Hz, 1 H, H_{arom}), 7.76 (dd, $^3J_{H,H}$ = 6.7 Hz, $^4J_{H,H}$ = 0.6 Hz, 1 H, H_{arom}), 7.64 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 0.6 Hz, 1 H, H_{arom}), 7.60 (dd, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,H}$ = 9.0 Hz, 1 H, H_{arom}), 5.21–5.16 (m, 1 H, CH), 2.28–2.21 (m, 2 H, β-CH_2), 1.90–1.84 (m, 2 H, β-CH_2), 1.38–1.18 (m, 16 H, 8 CH_2), 0.82 (t, $^3J_{H,H}$ = 7.0 Hz, 6 H, 2 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27.0 °C): δ = 163.4, 149.7, 149.6, 148.8, 148.2, 138.6, 135.4, 134.2, 131.9, 131.6, 130.0, 129.5, 129.1, 126.7, 126.4, 126.3, 124.3, 123.4, 123.1, 123.0, 116.7, 54.8, 32.4, 31.7, 29.2, 26.9, 22.6, 14.0.

MS (DEP/EI): *m*/*z* (%) = 767 (14) [M^+], 585 (100) [M^+ – $C_{13}H_{26}$].

HRMS: *m*/*z* [M]$^+$ calcd for $C_{48}H_{41}N_5O_5$: 767.3108; found: 767.3114.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 334.4 (12000), 459.8 (19500), 491.0 (53400), 528.1 nm (88900).

Fluorescence ($CHCl_3$) : λ_{max} (I_{rel}) = 534.7 (1.00), 577.2 nm (0.51).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 490 nm, $E_{490\ nm,\ 1\ cm}$ = 0.0140, reference **A** with Φ = 1.00): 0.98.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 350 nm, $E_{350\ nm,\ 1\ cm}$ = 0.0026, reference: **C** with Φ = 1.00): 1.00.

Anal. Calcd for $C_{48}H_{41}N_5O_5$ (767.3): C, 75.08; H, 5.38; N, 9.12. Found: C, 74.91; H, 5.36; N, 9.07.

2-[3-(2,1,3-Benzoxadiazol-4-yl)phenyl)-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (7a)

Following the typical procedure for **6c** using **4b** (44 mg, 0.21 mmol), **5a** (115 mg, 200 μmol), $Zn(OAc)_2$ (7.4 mg, 40 μmol), and quinoline (2.5 mL) to give **7a** as a red solid; yield: 122 mg (80%); mp 287–289 °C; R_f = 0.4 (CH_2Cl_2).

IR (ATR): 2925 (m), 1701 (s), 1661 (s), 1595 (m), 1343 (s), 1174 (m), 851 (m), 809 (s), 784 (s), 744 cm^{-1} (s).

^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 8.76–8.63 (m, 8 H, H_{per}), 8.20 (d, $^3J_{H,H}$ = 8.0 Hz, 1 H, H_{arom}), 8.08 (dd, $^4J_{H,H}$ = 1.9 Hz, $^4J_{H,H}$ = 1.9 Hz, 1 H, H_{arom}), 7.82 (d, $^3J_{H,H}$ = 9.0 Hz, 1 H, H_{arom}), 7.75 (dd, $^3J_{H,H}$ = 7.9 Hz, $^3J_{H,H}$ = 7.9 Hz, 1 H, H_{arom}), 7.69 (d, $^3J_{H,H}$ = 6.9 Hz, 1 H, H_{arom}), 7.51–7.47 (m, 2 H, H_{arom}), 5.22–5.16 (m, 1 H, CH), 2.29–2.22 (m, 2 H, β-CH_2), 1.92–1.85 (m, 2 H, β-CH_2), 1.39–1.19 (m, 16 H, 8 CH_2), 0.83 (t, $^3J_{H,H}$ = 6.9 Hz, 6 H, 2 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27 °C): δ = 163.5, 149.8, 148.4, 136.5, 135.8, 135.3, 134.2, 131.9, 131.7, 130.0, 129.8, 129.5, 129.3, 128.7, 128.7, 128.4, 126.7, 126.4, 123.4, 123.2, 123.1, 115.6, 54.8, 32.4, 31.8, 29.2, 26.9, 22.6, 14.0.

MS (DEP/EI): *m*/*z* (%) = 766 (37) [M^+], 584 (100) [$M^+ - C_{13}H_{26}$].

HRMS: *m*/*z* [M]$^+$ calcd for $C_{49}H_{42}N_4O_5$: 766.3157; found: 766.3160.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 338.1 (11800), 459.8 (18900), 491.0 (51500), 527.4 nm (85900).

Fluorescence ($CHCl_3$) : λ_{max} (I_{rel}) = 534.9 (1.00), 577.6 nm (0.50).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm,\ 1\ cm}$ = 0.0147, reference **A** with Φ = 1.00): 0.95.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 350 nm, $E_{350\ nm,\ 1\ cm}$ = 0.0035, reference: **C** with Φ = 1.00): 0.85.

Anal. Calcd for $C_{49}H_{42}N_4O_5$ (766.3): C, 76.74; H, 5.52; N, 7.31. Found: C, 76.44; H, 5.63; N, 7.26.

2-[4-(2,1,3-Benzothiadiazol-4-yl)phenyl]-9-(nonadecan-10-yl)anthra[2,1,9-*def*:6,5,10-*d′e′f′*]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (6b)

Following the typical procedure for **6a** using **3c** (45 mg, 0.20 mmol), 9-(1-nonyldecyl)-1*H*-isochromeno[6′,5′,4′:10,5,6]anthra[2,1,9-*def*]isoquinoline-1,3,8,10(9*H*)-tetraone (**5b**; 132 mg, 200 μmol), $Zn(OAc)_2$ (7.4 mg, 40 μmol), and quinoline (2.5 mL) to give **6b** as an amorphous red material; yield: 128 mg (74%); mp 278–281 °C (dec.); R_f = 0.3 (silica gel, CH_2Cl_2).

IR (ATR): 2921 (m), 1695 (s), 1650 (s), 1593 (s), 1342 (s), 1253 (s), 864 (m), 810 (s), 793 (s), 746 cm^{-1} (s).

^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 8.77–8.63 (m, 8 H, H_{per}), 8.17 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, H_{arom}), 8.04 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 1.0 Hz, 1 H, H_{arom}), 7.79 (dd, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 1.0 Hz, 1 H, H_{arom}), 7.72 (dd, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,H}$ = 8.7 Hz, 1 H, H_{arom}), 7.52 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, H_{arom}), 5.21–5.15 (m, 1 H, CH), 2.28–2.20 (m, 2 H, β-CH_2), 1.90–1.82 (m, 2 H, β-CH_2), 1.38–1.13 (m, 28 H, 14 CH_2), 0.82 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, 2 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27.0 °C): δ = 163.6, 155.6, 153.4, 137.8, 135.2, 134.3, 133.6, 131.9, 130.3, 129.9, 129.6, 128.8, 128.1, 126.7, 126.4, 123.3, 123.3, 123.1, 120.9, 54.8, 32.3, 31.8, 29.5, 29.3, 27.0, 22.6, 14.1.

MS (DEP/EI): *m*/*z* (%) = 866 (11) [M^+], 600 (100) [$M^+ - C_{19}H_{38}$].

HRMS: *m*/*z* [M]$^+$ calcd for $C_{55}H_{54}N_4O_4S$: 866.3866; found: 866.3863.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 315.9 (19300), 351.1 (12100), 459.8 (21000), 491.0 (55800), 527.4 nm (92500).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 534.6 (1.00), 577.5 (0.50), 625.5 nm (0.12).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 491 nm, $E_{491\ nm,\ 1\ cm}$ = 0.0129, reference **A** with Φ = 1.00): 1.00.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 353 nm, $E_{353\ nm,\ 1\ cm}$ = 0.0024, reference **C** with Φ = 1.00): 1.00.

Anal. Calcd for $C_{55}H_{54}N_4O_4S$ (866.4): C, 76.18. 6.28; N, 6.46; S, 3.70. Found: C, 75.62; H, 6.26; N, 6.41; S, 3.54.

6-[3-(2,1,3-Benzoxadiazol-4-yl)phenyl]-2,10-bis(1-hexylheptyl)-1*H*-pyrrolo[3′4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone (10a); Typical Procedure

Aniline **4b** (35 mg, 0.17 mmol), *N*,*N*′-bis(1-hexylheptyl)benzo[*ghi*]perylene-2,3,8,9,11,12-hexacarboxylic-2,3:8,9-bis(dicarboximide)-11,12-anhydride (**8a**; 103 mg, 121 μmol), and quinoline (2.0 mL) were stirred under argon and microwave radiation (180 W) at 210 °C for 5 h (dark yellow mixture). The mixture was allowed to cool, added dropwise with intense stirring to 2 M aq HCl (300 mL), stirred for 2 h, and allowed to stand for 16 h. The product was collected by vacuum filtration, washed with 2 M aq HCl (300 mL), hot distilled H_2O (300 mL) and MeOH–H_2O (1:1, 300 mL), and dried at 110 °C in vacuo for 2 d. The residue was dissolved in the minimal amount of CH_2Cl_2 and purified by column chromatography (short column with alumina, CH_2Cl_2 and a further column with silica gel, CH_2Cl_2, brightly yellow first fraction) to give **10a** as a yellow solid; yield: 94 mg (75%); mp >300 °C; R_f = 0.9 ($CHCl_3$).

IR (ATR): 2926 (m), 1710 (s), 1662 (s), 1366 (s), 1318 (s), 812 (m), 764 (m), 748 cm^{-1} (m).

^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 10.34–10.18 (m, 2 H, H_{bper}), 9.16–9.02 (m, 4 H, H_{bper}), 8.48 (s, 1 H, H_{arom}), 8.28 (m, 1 H, H_{arom}), 7.95–7.91 (m, 1 H, H_{arom}), 7.88–7.85 (m, 2 H, H_{arom}), 7.82 (dd, $^3J_{H,H}$ = 7.9 Hz, $^3J_{H,H}$ = 7.9 Hz, 1 H, H_{arom}), 7.58 (dd, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,H}$ = 8.8 Hz, 1 H, H_{arom}), 5.34–5.26 (m, 2 H, CH), 2.40–2.32, (m, 4 H, β-CH_2), 2.03–1.96 (m, 4 H, β-CH_2), 1.49–1.22 (m, 32 H, 16 CH_2), 0.83 (t, $^3J_{H,H}$ = 7.0 Hz, 12 H, 4 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27.0 °C): δ = 166.7, 149.8, 148.5, 136.4, 132.0, 131.9, 129.8, 128.9, 128.5, 127.3, 127.2, 126.2, 123.6, 115.6, 55.4, 32.3, 31.8, 29.3, 27.1, 22.6, 14.0.

MS (DEP/EI): *m*/*z* (%) = 1042 (6) [M^+ + H], 678 (100) [M^+ + H – 2·$C_{13}H_{26}$].

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{66}H_{68}N_5O_7$: 1042.5041; found: 1042.5070.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 315.9 (23400), 330.7 (23500), 381.2 (40900), 411.6 (15700), 436.8 (37300), 467.3 nm (57100).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 476.3 (1.00), 511.2 nm (0.80).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 437 nm, $E_{437\ nm,\ 1\ cm}$ = 0.0152, reference **B** with Φ = 1.00): 0.12.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 350 nm, $E_{350\ nm,\ 1\ cm}$ = 0.0109, reference **C** with Φ = 1.00): 0.12.

Anal. Calcd for $C_{66}H_{67}N_5O_7$ (1041.5): C, 76.06; H, 6.48; N, 6.72. Found: C, 75.89; H, 6.43; N, 6.70.

2-(4,7-Dibromo-2,1,3-benzothiadiazol-5-yl)-9-(1-hexylheptyl)anthra[2,1,9-*def*:6,5,10-d′e′f′]diisoquinoline-1,3,8,10(2*H*,9*H*)-tetraone (15; Figure 9)

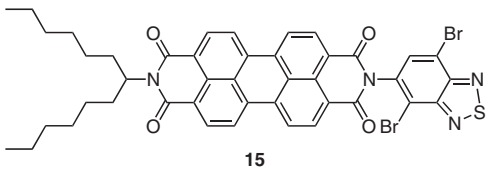


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Figure 9

Following the typical procedure for **6c** using 4,7-dibromo-2,1,3-benzothiadiazol-5-amine (63 mg, 0.20 mmol), **5a** (115 mg, 200 μmol), $Zn(OAc)_2$ (7.4 mg, 40 μmol), and quinoline (2.0 mL) and then purification by dissolving the material in the minimal amount of CH_2Cl_2 and purification by column chromatography (short column with neutral alumina, CH_2Cl_2–MeOH, 100:1 and a further column with silica gel, CH_2Cl_2, deeply red first fraction) to

give the product as a red solid; yield: 119 mg (69%); mp 185 °C (dec.); R_f = 0.6 (CH_2Cl_2).

IR (ATR): 2923 (w), 1655 (s), 1592 (s), 1339 (s), 1250 (s), 853 (m), 810 (s), 802 (m), 746 (s), 728 cm^{-1} (m).

^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 8.80–8.67 (m, 8 H, H_{per}), 7.90 (s, 1 H, H_{arom}), 5.22–5.16 (m, 1 H), 2.29–2.21 (m, 2 H), 1.93–1.84 (m, 2 H), 1.39–1.19 (m, 16 H), 0.83 (t, ^3J = 7.0 Hz, 6 H).

^{13}C NMR (150 MHz, $CDCl_3$, 27.0 °C): δ = 162.4, 153.2, 152.8, 136.9, 135.9, 134.0, 133.3, 132.3, 131.9, 131.2, 130.2, 129.5, 126.9, 126.3, 123.7, 123.1, 122.4, 115.8, 114.1, 54.9, 32.4, 31.7, 29.2, 26.9, 22.6, 14.0.

MS (DEP/EI): *m*/*z* (%) = 862 (9) [M^+], 602 (100) [$M^+ - C_{13}H_{26} - Br$].

HRMS: *m*/*z* [M]$^+$ calcd for $C_{43}H_{36}Br_2N_4O_4S$: 862.0824; found: 862.0826.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 306.6 (13700), 315.9 (16600), 352.0 (8000), 367.8 (7500), 461.3 (19200), 492.5 (53300), 528.8 nm (88700).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 537.3 (1.00), 579.7 nm (0.52).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 492 nm, $E_{492\ nm,\ 1\ cm}$ = 0.0137, reference **A** with Φ = 1.00): 0.94.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 492 nm, $E_{492\ nm,\ 1\ cm}$ = 0.0137, reference **C** with Φ = 1.00): 0.96.

Anal. Calcd for $C_{43}H_{36}Br_2N_4O_4S$ (862.1): C, 59.73; H, 4.20; N, 6.48; S, 3.71. Found: C, 59.48; H, 4.30; N, 6.42; S, 3.76.

6-[4-(2,1,3-Benzoxadiazol-4-yl)phenyl]-2,10-bis(1-hexylheptyl)-1*H*-pyrrolo[3′4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone (9b)

Following the typical procedure for **10a** using 4-(2,1,3-benzoxadiazol-4-yl)aniline (**3d**; 21 mg, 0.10 mmol), **8a** (85 mg, 0.10 mmol), and quinoline (1.8 mL) gave **9b** as a yellow solid; yield: 77 mg (74%); mp >300 °C; R_f = 0.7 (CH_2Cl_2).

IR (ATR): 3077 (w), 2924 (m), 1712 (s), 1662 (s), 1375 (s), 1364 (s), 1308 (s), 846 (w), 811 (s), 747 cm^{-1} (m).

^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 10.37–10.23 (m, 2 H, H_{bper}), 9.19– 9.03 (m, 4 H, H_{bper}), 8.32 (d, $^3J_{H,H}$ = 8.6 Hz, 2 H, H_{arom}), 7.98 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, H_{arom}), 7.87 (dd, $^3J_{H,H}$ = 9.0 Hz, $^4J_{H,H}$ = 0.5 Hz, 1 H, H_{arom}), 7.75 (d, $^3J_{H,H}$ = 6.3 Hz, 1 H, H_{arom}), 7.58 (dd, $^3J_{H,H}$ = 6.6 Hz, $^3J_{H,H}$ = 9.0 Hz, 1 H, H_{arom}), 5.32–5.26 (m, 2 H, CH), 2.41–2.31 (m, 4 H, β-CH_2), 2.03–1.95 (m, 4 H, β-CH_2), 1.50–1.22 (m, 32 H, 16 CH_2), 0.82 (t, $^3J_{H,H}$ = 7.1 Hz, 12 H, 4 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27.0 °C): δ = 166.7, 149.9, 148.5, 135.0, 132.6, 132.2, 131.8, 129.5, 129.2, 128.5, 127.4, 127.0, 126.6, 124.4, 123.7, 122.8, 115.6, 55.4, 32.4, 31.8, 29.3, 27.1, 22.6, 14.0.

MS (DEP/EI): *m*/*z* (%) = 1042 (6) [M^+ + H], 678 (100) [M^+ + H – 2·$C_{13}H_{26}$].

HRMS: *m*/*z* [M + H]$^+$ calcd for $C_{66}H_{68}N_5O_7$: 1042.5041; found: 1042.5070.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 330.7 (26600), 381.2 (39600), 410.1 (19400), 436.8 (37600), 467.3 nm (56500).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 475.4 (1.00), 506.4 nm (0.79).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 437 nm, $E_{437\ nm,\ 1\ cm}$ = 0.0241, reference **C** with Φ = 1.00): < 0.01.

Anal. Calcd for $C_{66}H_{67}N_5O_7$ (1041.5): C, 76.06; H, 6.48; N, 6.72. Found: C, 75.93; H, 6.49; N, 6.73.

6-[5-(2,1,3-Benzoxadiazol-4-yl)pyridin-2-yl)-2,10-bis(1-hexylheptyl)-1*H*-pyrrolo[3′4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone (9d)

Following the typical procedure for **10a** using **3f** (21 mg, 0.10 mmol), **8a** (85 mg, 0.10 mmol), and quinoline (1.8 mL) with purification by column chromatography (basic alumina, $CHCl_3$–MeOH, 80:1, first brightly yellow shining main fraction) gave **9d** as a yellow solid; yield: 80 mg (77%); mp >300 °C; R_f = 0.3 (CH_2Cl_2).

IR (ATR): 3077 (w), 2924 (m), 1705 (m), 1659 (s), 1365 (s), 1318 (s), 846 (m), 812 (m), 748 cm^{-1} (m).

^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 10.56–10.48 (m, 2 H, H_{bper}), 9.41 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, H_{bper}), 9.34 (dd, $^4J_{H,H}$ = 2.5 Hz, $^5J_{H,H}$ = 0.4 Hz, 1 H, H_{arom}), 9.25–9.15 (m, 2 H, H_{bper}), 8.76 (dd, $^3J_{H,H}$ = 8.2 Hz, $^4J_{H,H}$ = 2.5 Hz, 1 H, H_{arom}), 7.95 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, H_{arom}), 7.95 (d, $^3J_{H,H}$ = 6.4 Hz, 1 H, H_{arom}), 7.80 (d, $^3J_{H,H}$ = 6.4 Hz, 1 H, H_{arom}), 7.63 (dd, $^3J_{H,H}$ = 6.6 Hz, ^3J = 9.0 Hz, 1 H, H_{arom}), 5.15–5.27 (m, 2 H, CH), 2.40–2.28 (m, 4 H, β-CH_2), 2.01–1.91 (m, 4 H, β-CH_2), 1.46–1.17 (m, 32 H, 16 CH_2), 0.81 (t, $^3J_{H,H}$ = 7.1 Hz, 12 H, 4 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27.0 °C): δ = 166.2, 149.7, 148.6, 148.3, 146.1, 138.5, 132.9, 131.7, 131.1, 129.0, 127.8, 127.6, 126.8, 126.4, 124.8, 123.9, 123.0, 122.3, 116.6, 55.4, 32.4, 31.8, 29.3, 27.1, 22.6, 14.0.

MS (DEP/EI): *m*/*z* (%) = 1042 (10) [M^+], 861 (45) [M^+ + 1 – $C_{13}H_{26}$], 679 (100) [$M^+ - 2\cdot C_{13}H_{26}$].

HRMS: *m*/*z* [M]$^+$ calcd for $C_{65}H_{66}N_6O_7$: 1042.4993; found: 1042.4981.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 330.4 (26900), 380.4, (49000), 410.9 (16200), 436.8 (38500), 467.3 nm (59400).

Fluorescence ($CHCl_3$) : λ_{max} (*I*) = 477.2 (1.00), 510.6 nm (0.73).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 436 nm, $E_{436\ nm,\ 1\ cm}$ = 0.0242, reference **C** with Φ = 1.00): 0.25.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 443 nm, $E_{443\ nm,\ 1\ cm}$ = 0.0183, reference **B** with Φ = 1.00): 0.24.

Anal. Calcd for $C_{65}H_{66}N_6O_7$ (1042.5): C, 74.83; H, 6.38; N, 8.06; found: C, 74.97; H, 6.60; N, 7.91.

6-(5-(2,1,3-Benzothiadiazol-4-yl)pyridin-2-yl)-2,10-bis(1-hexylheptyl)-1*H*-pyrrolo[3′4′:4,5]pyreno[2,1,10-*def*:7,8,9-*d′e′f′*]diisoquinoline-1,3,5,7,9,11(2*H*,6*H*,10*H*)-hexone (9c)

Following the typical procedure for **10a** using **3e** (23 mg, 0.10 mmol), **8a** (94 mg, 0.11 mmol), and quinoline (1.0 mL) at 210 °C for 3 h with purification by column chromatography (basic alumina, $CHCl_3$–MeOH, 80:1, first brightly yellow shining main fraction) gave **9c** as a yellow solid; yield: 79 mg (75%); mp >300 °C; R_f = 0.3 (CH_2Cl_2).

IR (ATR): 3082 (w), 2926 (m), 1718 (s), 1705 (s), 1661 (s), 1366 (s), 1319 (s), 851 (m), 812 (s), 749 cm^{-1} (m).

^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 10.51–10.39 (m, 2 H, H_{bper}), 9.33–9.29 (m, 3 H, H_{bper}, H_{arom}), 9.22–9.12 (m, 2 H, H_{bper}), 8.76 (dd, $^3J_{H,H}$ = 8.1 Hz, $^4J_{H,H}$ = 2.5 Hz, 1 H, H_{arom}), 8.14 (dd, $^3J_{H,H}$ = 8.8 Hz, $^4J_{H,H}$ = 1.0 Hz, 1 H, H_{arom}), 8.01 (d, $^3J_{H,H}$ = 8.1 Hz, 1 H, H_{arom}), 7.91 (dd, $^3J_{H,H}$ = 6.8 Hz, $^4J_{H,H}$ = 0.9 Hz, 1 H, H_{arom}), 7.80 (dd, $^3J_{H,H}$ = 6.8 Hz, $^3J_{H,H}$ = 8.8 Hz, 1 H, H_{arom}), 5.37–5.26 (m, 2 H), 2.43–2.29 (m, 4 H, β-CH_2), 2.03–1.92 (m, 4 H, β-CH_2), 1.49–1.19 (m, 32 H, 16 CH_2), 0.83 (t, $^3J_{H,H}$ = 7.1 Hz, 12 H, 4 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27.0 °C): δ = 166.4, 155.6, 153.2, 149.5, 145.4, 139.2, 133.2, 133.1, 130.1, 129.6, 128.3, 128.0, 127.6, 127.0, 124.9, 124.0, 123.2, 121.9, 55.3, 32.4, 31.8, 29.3, 27.0, 22.6, 14.0.

MS (DEP/EI): *m*/*z* (%) = 1059 (9) [M^+ + H], 877 (32) [M^+ + H – $C_{13}H_{26}$], 695 (79) [M^+ + H – 2·$C_{13}H_{26}$].

HRMS: *m*/*z* [M – H]$^+$ calcd for $C_{65}H_{65}N_6O_6S$: 1057.4686; found: 1057.4731.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 265.0 (38200), 315.6 (33400), 380.0, (44900), 410.8 (17000), 437.0 (39400), 467.0 nm (59200).

Fluorescence ($CHCl_3$): λ_{max} (I_{rel}) = 476.3 (1.00), 509.7 nm (0.75).

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 437 nm, $E_{437\ nm,\ 1\ cm}$ = 0.0352, reference **C** with Φ = 1.00): 0.27.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 437 nm, $E_{437\ nm,\ 1\ cm}$ = 0.0352, reference **B** with Φ = 1.00): 0.26.

Anal. Calcd for $C_{65}H_{66}N_6O_6S$ (1058.5): C, 73.70; H, 6.28; N, 7.93; S, 3.03. Found: C, 73.72; H, 6.37; N, 7.80; S, 3.08.

8-[4-(2,1,3-Benzothiadiazol-4-yl)phenyl]-2-(1-hexylheptyl)-1*H*-benzo[5,10]anthra[2,1,9-*def*]isoquinoline-1,3(2*H*)-dione (14)

Dry LiCl (42 mg, 1.0 mmol), Mg (24 mg, 1.0 mmol), and dry $ZnCl_2$ (136 mg, 1.00 mmol) in anhyd THF (2 mL) under argon were treated with 4-(4-iodophenyl)-2,1,3-benzothiadiazole (**3h**; 169 mg, 268 μmol) and the mixture was stirred at 20 °C for 2 h. The soln was separated from the residual Mg (argon atmosphere), treated with a mixture of $Pd(dba)_2$ (6 mg, 10 μmol), $(furyl)_3P$ (5 mg, 22 μmol), and 8-iodo-2-(1-hexylheptyl)-1*H*-benzo[5,10]anthra[2,1,9-*def*]isoquinoline-1,3(2*H*)-dione (**13**; 120 mg, 191 μmol) in anhyd THF (1 mL), and stirred at 20 °C for 1 h. The reaction was quenched by the addition of sat. aq NH_4Cl soln (10 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were dried ($MgSO_4$), and evaporated in vacuo. The residue was dissolved in the minimal amount of $CHCl_3$–MeOH (80:1) and purified by column chromatography (short column neutral alumina, $CHCl_3$–MeOH, 80:1, and then silica gel, $CHCl_3$ and finally silica gel, toluene, deep red band) to give **14** as a red solid; yield: 14 mg (7%); mp 169–170 °C; R_f = 0.4 (silica gel, toluene).

IR (ATR): 2923 (m), 1687 (s), 1646 (s), 1353 (s), 1292 (m), 1202 (m), 853 (m), 807 (s), 751 cm^{-1} (s).

^1H NMR (600 MHz, $CDCl_3$, 27 °C, TMS): δ = 8.64–8.55 (m, 2 H, H_{per}), 8.51 (d, $^3J_{H,H}$ = 7.9 Hz, 1 H, H_{per}), 8.48 (d, $^3J_{H,H}$ = 7.2 Hz, 1 H, H_{per}), 8.45 (dd, $^3J_{H,H}$ = 6.7 Hz, $^3J_{H,H}$ = 8.1 Hz, 2 H, H_{per}), 8.14–8.10 (m, 3 H), 8.06 (dd, $^3J_{H,H}$ = 8.7 Hz, $^4J_{H,H}$ = 1.1 Hz, 1 H, H_{arom}), 7.82 (dd, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 1.1 Hz, 1 H, H_{arom}), 7.75 (dd, $^3J_{H,H}$ = 6.9 Hz, $^3J_{H,H}$ = 8.7 Hz, 1 H, H_{arom}), 7.71 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, H_{arom}), 7.66 (d, $^3J_{H,H}$ = 7.7 Hz, 1 H, H_{arom}), 7.61 (dd, $^3J_{H,H}$ = 7.5 Hz, $^3J_{H,H}$ = 8.3 Hz, 1 H, H_{arom}), 5.23–5.18 (m, 1 H, CH), 2.29–2.23 (m, 2 H, β-CH_2), 1.88–1.83 (m, 2 H, β-CH_2), 1.38–1.18 (m, 16 H, 8 CH_2), 0.82 (t, $^3J_{H,H}$ = 7.1 Hz, 6 H, 2 CH_3).

^{13}C NMR (150 MHz, $CDCl_3$, 27.0 °C): δ = 165.3, 164.2, 155.6, 153.5, 142.6, 140.0, 137.0, 133.9, 132.6, 130.8, 130.3, 130.0, 129.7, 129.5, 129.4, 129.1, 128.8, 128.4, 128.2, 127.9, 127.6, 127.0, 126.6, 123.3, 120.9, 129.6, 120.3, 120.1, 54.4, 32.4, 31.8, 29.3, 27.0, 22.6, 14.0.

MS (DEP/EI): *m/z* (%) = 713 (48) [M^+], 531 (100) [$M^+ - C_{13}H_{26}$].

HRMS: *m/z* $[M]^+$ calcd for $C_{47}H_{43}N_3O_2S$: 713.3076; found: 713.3082.

UV/Vis ($CHCl_3$): λ_{max} (ε) = 315.9 (15700), 356.7 (8700), 502.1 (40200), 518.5 nm (40200).

Fluorescence ($CHCl_3$): λ_{max} = 569.0 nm.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 498 nm, $E_{498\ nm,\ 1\ cm}$ = 0.0235, reference **A** with Φ = 1.00): 1.00.

Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 498 nm, $E_{498\ nm,\ 1\ cm}$ = 0.0235, reference **C** with Φ = 1.00): 1.00.

Anal. Calcd for $C_{47}H_{43}N_3O_2S$ (713.3): C, 79.07; H, 6.07; N, 5.89; S, 4.49. Found: C, 78.80; H, 6.10; N, 5.74; S, 4.82.

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