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Fluorescent aryl naphthalene dicarboximides with large Stokes shifts and strong solvatochromism controlled by dynamics and molecular geometry†

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A series of highly fluorescent 4-aryl substituted naphthalene dicarboximides were efficiently prepared *via* metal organic C–C-coupling reactions. The obtained push–pull fluorophores display a distinct positive solvatochromism of the fluorescence. These optical properties are shown to be significantly dependant on the molecular geometry. Corresponding to TICT, a twist between the donor and the acceptor moiety enhances the intramolecular charge transfer resulting in such pronounced solvatochromism. Complete orthogonalisation inhibits the fluorescence. An intentional skew arrangement leads to solvent-adjustable chromophores with high fluorescence quantum yields and Stokes shifts of more than 1.6 eV.

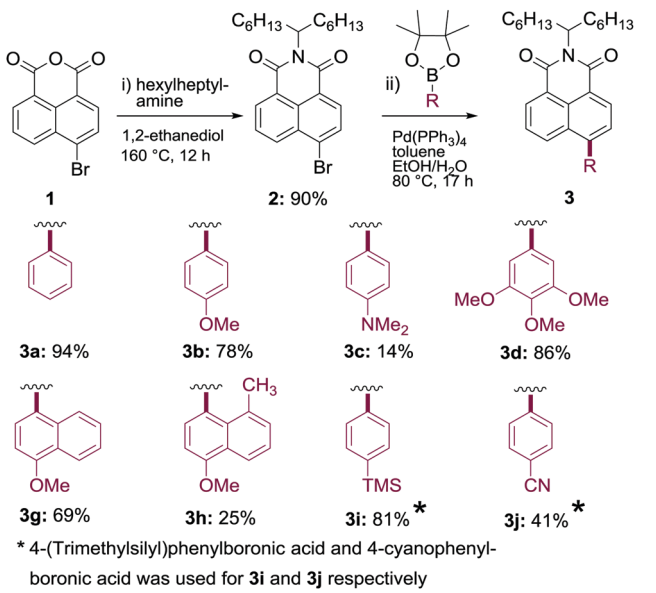
Introduction

peri-Naphthylcarboximides[1] are well known fluorescent dyes which find broad applications like in white light-emitting diodes.[2] Naphthalimides with donor groups in position 4 such as 4-amino-naphthalene-1,8-dicarboximides[3] and 4-alkoxy-naphthalene-1,8-carboximides[4] are of special interest since comparably large Stokes shifts and positive solvatochromism[5] of the fluorescence are observed. A photo-induced shift of electron density from the donor to the carboximide is responsible for inducing a large dipole moment. Lowering of the energy of the excited state by solvation with polar solvents causes a bathochromic shift of the fluorescence. This process corresponds to the positive solvatochromism of 4-amino-*N*-methylphthalimide applied for Zelinskii's[6] solvent polarity *S* scale. An even more pronounced solvatochromism of naphthalimides should be obtained through the introduction of extended electron rich aryl moieties.

Results and discussion

The fluorescent solvatochromism is expected to increase with the photo-induced dipole moment depending on the distance of the separated charges. Therefore, we inserted aryl groups as conjugating spacers between the donor groups and the naphthalimide acceptor moiety to achieve such a prolongation. However, little is known about such 4-aryl naphthalimides.[7] We targeted their synthesis by means of transition metal-mediated arylations. To obtain highly soluble dyes, we started with a condensation of readily available 4-bromonaphthalic anhydride **1** with tridecan-7-amine[8] giving the highly soluble key intermediate **2** (Scheme 1). The Suzuki cross-coupling reaction of **2** with various aryl dioxaborolanes gave the corresponding arylated derivatives **3a–d** and **3g–j**, respectively.

Substitution with the sterically hindered 2,6-dimethyl phenyl boronate failed where synthesis could be alternatively realised by the stepwise peripheral introduction of the sterically demanding



Scheme 1 Synthesis of arylated naphthalene carboximides; (i) amine condensation; (ii) Suzuki cross-coupling.

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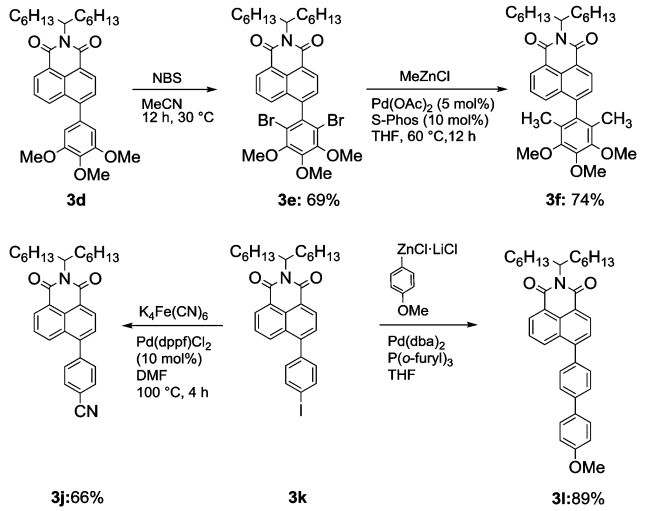

Scheme 2 Bromination of **3d** and subsequent cross-coupling with MeZnCl giving **3f** (top); cyanation and Negishi cross-coupling of **3k** leading to **3j** and **3l** respectively (bottom).

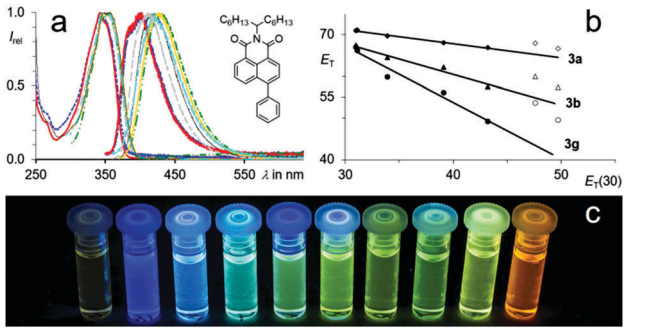

Fig. 1 (a) UV/Vis absorption (left) and fluorescence (right) spectra of **3a** in various solvents. From left to right: *n*-hexane (thick solid red), *n*-tetradecane (dotted blue), toluene (dashed grey), chloroform (solid black), 1-undecanol (dotted dashed turquoise) DMF (diffuse yellow), 1-butanol (double dotted dashed). (b) Linear relationship of the solvatochromism (E_T) of **3a** (diamonds), **3b** (triangles) and **3g** (circles), respectively to the $E_T(30)$ solvent polarity scale. Closed symbols: aprotic solvents; open symbols: protic solvents, neglected for regression. Scales are in kcal mol^{-1}. (c) Aryl naphthalene carboximides **3** in $CHCl_3$ under UV-light (366 nm). From left to right: **3f**, **3j**, **3b**, **3l**, **3a**, **3i**, **3h**, **3g**, **3d**, **3c**.

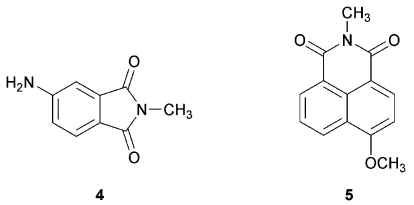

Fig. 2 4-Amino-*N*-methylphthalimide (**4**) and 4-methoxy-*N*-methylnaphthalimide (**5**) as reference for fluorescence data comparison.

methyl groups. The easily accessible trimethoxy derivative **3d** was brominated with *N*-bromosuccinimide to give **3e** and then further treated with methylzinc chloride under typical Negishi cross-coupling conditions[9] to provide **3f** (Scheme 2). Since also the borylation of more complex aryl halides proved to be difficult, we converted the trimethylsilyl derivative **3i** to the corresponding aryl iodide **3k** in order to extend the conjugated system. A typical Negishi cross-coupling of **3k** with *p*-anisylzinc chloride[10] (prepared from the reaction of 4-iodoanisole with iPrMgCl·LiCl, followed by $ZnCl_2$) gave the methoxy biphenyl derivative **3l** in very good yield. Further, the cyanation of **3k** led to the corresponding arylnaphthyl cyanide **3j** in an improved yield (Scheme 2).

From UV/Vis and fluorescence measurements it can be clearly recognized that our new dyes **3** are moderately solvatochromic in absorption (Fig. S24 and S26–S34, ESI†) and strongly solvatochromic in fluorescence as shown for the simple phenyl derivative **3a** (Fig. 1a and Fig. S25, ESI†). This indicates an optical excitation-induced increase of the dipole moment and was subject of further investigations. The molar energies of fluorescence light of various carboximides were calculated by means of eqn (1) where λ_{max} is the fluorescence maximum of the individual dye in the tested solvent (E_T values[11] are in kcal mol^{-1} for comparison with previously reported values in the literature to avoid confusion; these may be multiplied by 4.2 to obtain SI units). The solvatochromism of the carboximides was analysed according to various theoretical approaches. Those of Kawski,[12] Kamlet, Taft and Abboud[13] or Catalán[14] fitted our experimental results well. The respective analyses are found in the supporting information in Chapter 4. Furthermore, we investigated the fluorescent solvatochromism in more detail using the concepts of Brooker's χ_R scale[15] and Dimroth and Reichardt's $E_T(30)$ polarity scale[11] which delivered the best results. The first represents mainly the polarisability of the solvent whereas the second indicates mostly the effect of dynamic solvation. The spectroscopic data of dyes **3** were compared to reported data to evaluate the solvent sensitivity of the fluorescence. The highly solvatochromic 4-amino-*N*-methylphthalimide (**4**) as the basis of Zelinskii's universal *S* solvent polarity scale[6] served as reference as well as the simple donor substituted 4-amino-*N*-methylnaphthalimide (**5**) (Fig. 2). The E_T values of **4** were calculated from literature data for various solvents. A linear free energy relation (LFER)[16] of these E_T values with the $E_T(30)$ polarity scale according to eqn (2) gave appreciably better results (correlation number $r = 0.95$ for $n = 14$ solvents) than with Brooker's χ_R scale ($r = 0.90$ for $n = 14$).

$$E_T = 28\,591/\lambda_{max} \quad (1)$$

$$E_T = a \cdot E_T(30) + b \quad (2)$$

Similar results were obtained for the solvatochromism of the fluorescence of **3** (Table 1). As a consequence, we conclude that the solvent effects by polar dynamic orientation of the solvent molecules dominate for the reported carboximides and agreed with the $E_T(30)$ scale as most appropriate comparison.

We investigated the solvents *n*-tetradecane, *n*-hexane, toluene, chloroform, *N*,*N*-dimethyl formamide (DMF), 1-undecanol and 1-butanol for an overview of solvent effects where the two protic solvents were applied for studying the influence of hydrogen bonds. Linear correlations of the E_T values with the $E_T(30)$

Table 1 Solvatochromism of the fluorescence of the carbox-imides **3**, **4** and **5**

Dye	Φ^a	τ^b	α^c	r
4			−0.60	−0.95
5			−0.27	−0.89
3a	0.78	3.21	−0.34	−0.99
3b	0.83	4.11	−0.74	−0.99
3c	0.64	6.99	−1.49	−0.96
3d	0.65	6.62	−1.43	−0.98
3f	<0.05			
3g	0.39	4.07	−1.36	−0.98
3h	0.40	4.14	−1.37	−0.99
3i	0.79	3.08	−0.34	−0.99
3j	0.54	1.34	−0.80	−0.99
3l	0.67	2.93	−1.33	−0.98

Applied solvents: *n*-tetradecane, *n*-hexane, toluene, chloroform, dimethylformamide (DMF). [a] Fluorescence quantum yield Φ in chloroform. [b] Fluorescence lifetime τ in ns in chloroform. [c] Slope α of the linear regression. [d] Coefficient r of correlation for applications of eqn (2).

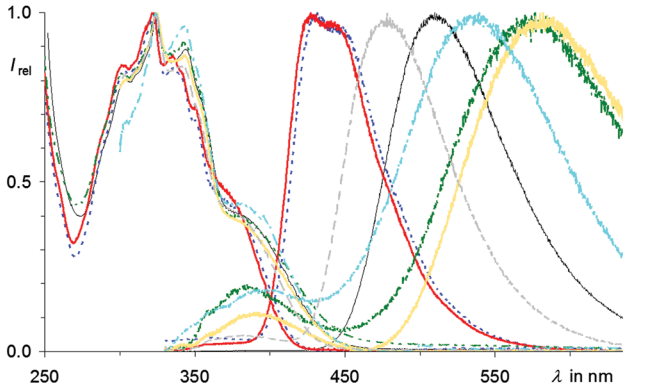

Fig. 3 UV/Vis absorption (left) and fluorescence (right) spectra of **3g** in various solvents. From left to right: *n*-hexane (thick solid red curves), *n*-tetradecane (dotted blue curves), toluene (dashed grey curves), chloroform (thin solid black curves), 1-undecanol (dotted dashed turquoise curves) DMF (diffuse yellow curves), 1-butanol (double dotted dashed green curves).

values were obtained. Larger deviations to higher E_T were observed for hydrogen bond-donating solvents such as 1-butanol and 1-undecanol indicating the specific influence of such interactions; the solvent viscosity seems to have a minor influence (compare hexane with tetradecane and 1-butanol with 1-decanol) and large Stokes shifts are even observed in a solid glassy matrix of PMMA. As a consequence, the further discussion was concentrated on the non-hydrogen bond-donating solvents for better comparability between the dyes **3–5**. A slope α of −0.60 is found for 4-amino-*N*-methylphthalimide (dye **4**, Table 1) and characterises the sensitivity of this highly solvatochromic fluorescent dye to polar solvent effects. In comparison, this interaction is appreciably lower for the methoxynaphthalimide **5** (α = −0.27) and indicates a smaller alteration of the molecular dipole moment with optical excitation. An extension of the conjugated system of the naphthalimide with a phenyl group in **3a** increases the slope slightly to α = −0.34 (Fig. 1b). Further introduction of a donor group into the *p*-position of the phenyl substituent to obtain **3b** establishes a donor acceptor system between the methoxy- and the carbonyl groups and enhances the sensitivity (α = −0.74) to exceed the solvatochromism of **4** by far. The dimethylamino group of derivative **3c** causes an even higher sensitivity towards solvents, however, the fluorescence quantum yield strongly decreases in polar solvents. Multiple donor groups as in **3d** also display a remarkably high solvatochromism with comparably high fluorescence quantum yields; even though weak fluorescence was still observed in polar DMF. A substitution with larger aryl groups like the 4-methoxynaphthyl moiety leads to **3g** which displays a very distinct solvatochromism (α = −1.36) while still exhibiting high fluorescence quantum yields in polar solvents. Further extension of the conjugated framework to the methoxybiphenyl derivative **3l** also induces such a pronounced fluorescent solvatochromism (α = −1.33) exceeding that of the anisyl-substituted species **3b**.

Finally, the effect of the donor acceptor motif in **3b** was further tested with **3j** where the electron donating methoxy group was exchanged by an electron withdrawing cyano moiety. There is still a comparably high sensitivity to solvent polarity, but as expected, the effect of the donor-substituted derivatives was not reached (Table 1). The electronic properties of the 4-methoxynaphthyl derivative **3g** are comparable to those of compound **3b**. However, the slope parameter α is found to be nearly twice as much. This observation made us focussing more intensely on the geometrical arrangement of the chromophores and prompted us to investigate the influence of steric hindrance on mesomerism. In comparison, the optical properties of **3g** (Fig. 3) and its methylated analogue **3h** are only slightly different from each other (Fig. S35, ESI†). This indicates a similar intramolecular geometry.

A skew arrangement of the aromatic systems seems to be mainly influenced by *peri* hydrogen atoms of the naphthalene subunits. These findings were further confirmed by quantum-chemical DFT calculations (B3LYP 6-311**G) as shown in Table 2, Fig. 4 and Table S10, S11 (ESI†). Hence, the steric influence of the methyl group in **3h** is only subordinated (dihedral angle 77.38°)

Table 2 Optimized structures and calculated dipole moments of **3** (DFT B3LYP 6-311**G)

Dye	θ^a	$\theta_{ex}{}^b$	Dipole^c	Dipole$_{E1}{}^d$
3a	57.8	39.64	5.52	7.75
3b	55.61	35.86	6.40	9.82
3c	51.35	31.43	9.20	14.86
3d	57.34	35.67	6.77	9.22
3f	87.42	89.36	6.08	7.22
3g	71.60	43.34	6.47	12.21
3h	75.38	44.94	6.03	12.20
3i	57.31	36.39	6.01	8.53
3j	57.95	36.57	0.47	1.66
3l	56.66	32.24	6.94	11.26
	39.56[e]	31.92[e]		
4			5.20	8.92
5			6.29	7.96

Applied solvents: *n*-tetradecane, *n*-hexane, toluene, chloroform, dimethylformamide (DMF). [a] Calculated dihedral angle θ in the ground state. [b] Calculated dihedral angle θ in the first electronically excited state. [c] Dipole moment in the electronic ground state in Debye. [d] Dipole moment in the first electronically excited state in Debye. [e] Dihedral angle between phenyl moieties.

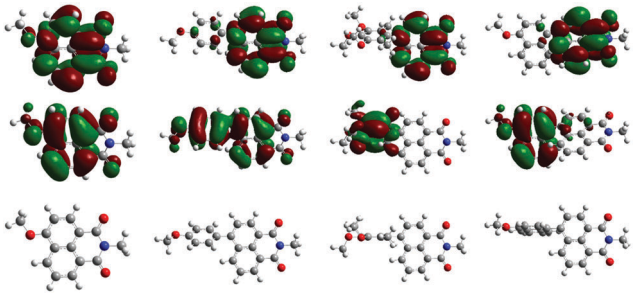

Fig. 4 Quantum chemical calculations. From bottom to top: lowest energy structures (ground state, B3LYP 6-311**G), HOMO (middle) and LUMO (top) orbitals. Left to right: **5**, **3b**, **3f**, **3g**.

and does not affect the geometry significantly (70.60° for **3g**). Comparison of the 3,4,5-trimethoxyphenyl naphthalimides **3d** (57.34°) and **3f** exhibits much more pronounced effects. The steric repulsion of the methyl groups in **3f** arranges the two aromatic systems statically fixed. The nearly orthogonal geometry (87.42°, Table 2 and Fig. 4) results in low fluorescence quantum yield of less than 0.05.

A twisted geometry between the donor and the acceptor promotes charge transfer causing strong solvatochromism in fluorescence and large Stokes shifts. Moderate angles below 80° preserve high fluorescence quantum yields. A complete orthogonalisation (**3f**) quenches fluorescence where an obviously essential residual orbital overlap is lacking. We further confirmed this concept by heating a solution of **3f** in diethylene glycol diethyl ether to 200 °C where the very weak fluorescence reversibly becomes intensified by a factor of 2 (Fig. S36, ESI†).[17] This is attributed to thermally induced vibronic perturbation of the nearly orthogonal arrangement enabling fluorescence. The proposed geometrical requirements for a distinct charge transfer are related to the TICT theory.[18] However, our results imply that orthogonal arrangements between the donor and the acceptor completely quench the fluorescence. Significant fluorescence is attributed to skew conformations which tend to more planar arrangements in the excited state allowing significant orbital overlap. Thus, the optical properties, particularly the fluorescent solvatochromism is not the result of a twist-induced charge transfer. It is rather the result of an interplay of conformational change and electronic charge transfer depending on the dipole moment. By tuning the molecular geometry we could obtain a series of chromophores with adjustable fluorescence and quantum yields of up to more than 80%.

Conclusions

In summary, we have reported new, readily soluble and highly fluorescent derivatives of naphthalene-1,8-dicarboximides that have been obtained by Pd-catalyzed arylation in position 4. These compounds display a pronounced solvatochromic fluorescence. The sensitivity of the substituted naphthalimides towards solvent polarity was evaluated according to several theoretical approaches. A photo-induced charge transfer from the electron rich aryl moiety to the naphthalimide is enhanced in polar solvents and causes a bathochromic shift of the fluorescence. Furthermore, the electronic effects are accompanied by molecular dynamics. The intramolecular arrangement influences the intensity of the charge transfer. A skew geometry between the donor and the acceptor allows planarization in the first electronically excited state. This allows high fluorescent quantum yields and still favours a pronounced charge transfer resulting in both distinct solvatochromism and large Stokes shifts. In contrast to basic TICT-theory, no orthogonalization occurs and rectangular orientation leads to strongly quenched fluorescence. The presented synergy of electronic and geometric effects results in highly fluorescent compounds such as **3b** and **3g** with easily adjustable emission spectra controlled by medium effects. This provides very large Stokes shifts exceeding 200 nm (approx. 1.6 eV) being of interest for various applications such as for frequency converters, fluorescence optical fibers and highly tunable light sources.

Experimental

General information on the experimental conduct and synthesis of precursors can be found in the ESI.†

6-Phenyl-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3a)

A Schlenk-flask was charged with 6-bromo-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (480 mg, 1.05 mmol, 1.0 equiv.) and 4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (265 mg, 1.30 mmol, 1.2 equiv.). Both compounds were dissolved in toluene (20 mL) under a light argon-stream. K_2CO_3 (2.76 g, 20.0 mmol) was dissolved in a mixture of water (10 mL) and EtOH (4 mL) and added to the Schlenk-flask followed by tetrakis(triphenylphosphine)palladium(0) (116 mg, 0.100 mmol, 10 mol%). The mixture was purged with argon for 30 min and then heated to 80 °C. The reaction mixture was stirred at this temperature for further 17 h. After cooling to room temperature, the organic phase was separated and the aqueous phase was extracted with toluene (3 × 10 mL). Purification by column chromatography (silica, iso-hexane/$CHCl_3$ = 1 : 1) gave compound **3a** as a bright yellow solid (450 mg, 94%). M.p.: 97 °C. IR (diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2919, 2852, 1696, 1653, 1587, 1396, 1348, 1237, 1176, 1100, 784, 768, 702. ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm = 8.69–8.56 (m, 2H), 8.25 (dd, J = 8.5, 1.1 Hz, 1H), 7.74–7.66 (m, 1H), 7.58–7.53 (m, 2H), 7.53–7.48 (m, 3H), 5.23–5.16 (m, 1H, NCH), 2.31–2.20 (m, 2H, β-CH_2), 1.89–1.80 (m, 2H, β-CH_2), 1.40–1.16 (m, 16H, 8 × CH_2), 0.83 (t, J = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm = 165.68, 165.48, 164.60, 164.41, 146.64, 139.04, 132.40, 131.70, 131.34, 130.91, 130.56, 130.08, 129.99, 129.00, 128.79, 128.56, 127.97, 126.97, 123.72, 123.00, 122.61, 121.88, 54.63, 32.58, 31.92, 29.39, 27.06, 22.74, 14.19. MS (EI, 70 eV) m/z (%): 455 (14) [M$^+$], 275 (22), 274 (100), 273 (22), 256 (12), 202 (8). HRMS (EI) for $C_{31}H_{37}NO_2$: calcd: 455.2824; found: 455.2820. EA for $C_{31}H_{37}NO_2$: calcd: C 81.72, N 3.07, H 8.19; found: C 81.52, N 3.10, H 8.31. UV/Vis ($CHCl_3$): λ_{max} (ε) = 355.4 nm (17 100). Fluorescence ($CHCl_3$, λ_{exc} = 355.4 nm): λ_{max} = 420.0 nm. Fluorescence quantum yield

($CHCl_3$, λ_{exc} = 355.4 nm, $E_{355.4nm,\ 1cm}$ = 0.134, reference: *N*,*N*′-bis(tridecan-7-yl)perylene-3,4:9,10-tetracarboxylic diimide with Φ = 1.00): Φ = 0.78.

6-(4-Methoxyphenyl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3b)

A Schlenk-flask was charged with 6-bromo-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (215 mg, 0.470 mmol, 1.04 equiv.) and 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (100 mg, 0.450 mmol, 1.0 equiv.). Both compounds were dissolved in toluene (10 mL) under a light argon-stream. K_2CO_3 (1.40 g, 10.0 mmol) was dissolved in a mixture of water (5 mL) and EtOH (1.00 mL) and added to the Schlenk-flask followed by tetrakis(triphenylphosphine)palladium(0) (20 mg, 0.018 mmol, 5 mol%). The mixture was purged with argon for 30 min and then heated to 80 °C. The reaction mixture was stirred at this temperature for further 17 h. After cooling to room temperature, the organic phase was separated and the aqueous phase was extracted with toluene (3 × 10 mL). Purification by column chromatography (silica, iso-hexane/$CHCl_3$ = 1 : 1) gave compound **3b** as an off-white solid (176 mg, 78%). M.p.: 63 °C. IR (diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2922, 2852, 1698, 1656, 1608, 1588, 1518, 1506, 1463, 1397, 1348, 1288, 1239, 1176, 1096, 1078, 1036, 963, 867, 838, 785, 760, 724. ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm = 8.66–8.52 (br s, 2H), 8.29 (dd, *J* = 8.5 Hz, 1.1 Hz, 1H), 7.72–7.63 (m, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.8 Hz, 2H), 5.26–5.13 (m, 1H, NCH), 3.90 (s, 3H, OCH_3), 2.33–2.17 (m, 2H, β-CH_2), 1.91–1.77 (m, 2H, β-CH_2), 1.42–1.11 (m, 16H, 8 × CH_2), 0.82 (t, *J* = 9.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm = 165.54, 164.54, 160.02, 146.43, 132.45, 131.30, 131.20, 130.17, 129.07, 127.86, 126.80, 123.70, 123.06, 122.18, 121.55, 114.28, 55.52, 54.55, 32.56, 31.89, 29.36, 27.03, 22.70, 14.15. MS (EI, 70 eV) *m*/*z* (%): 485 (23) [M^+], 316 (10), 304 (100), 303 (54), 286 (13), 198 (34), 180 (12). HRMS (EI) for $C_{32}H_{39}NO_3$: calcd: 485.2930; found: 485.2924. EA for $C_{32}H_{39}NO_3$: calcd: C 79.14, N 2.88, H 8.09; found: C 79.18, N 2.69, H 8.22. UV/Vis ($CHCl_3$): λ_{max} (ε) = 364.8 nm (16 900). Fluorescence ($CHCl_3$, λ_{exc} = 364.8 nm): λ_{max} = 459.6 nm. Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 364.8 nm, $E_{364.8nm,\ 1cm}$ = 0.252, reference: *N*,*N*′-bis(tridecan-7-yl)perylene-3,4:9,10-tetracarboxylic diimide with Φ = 1.00): Φ = 0.83.

6-(4-(Dimethylamino)phenyl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3c)

A Schlenk-flask was charged with 6-bromo-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (480 mg, 1.05 mmol, 1.05 equiv.) and *N*,*N*-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (247 mg, 1.00 mmol, 1.0 equiv.). Both compounds were dissolved in toluene (20 mL) under a light argon stream. K_2CO_3 (2.80 g, 20.0 mmol) was dissolved in a mixture of water (10 mL) and EtOH (3 mL) and added to the Schlenk-flask followed by tetrakis(triphenylphosphine)palladium(0) (115 mg, 0.100 mmol, 10 mol%). The mixture was purged with argon for 30 min and then heated to 80 °C. The reaction mixture was stirred at this temperature for further 17 h. After cooling to room temperature, the organic phase was separated and the aqueous phase was extracted with toluene (3 × 10 mL). Purification by column chromatography (silica, iso-hexane/$CHCl_3$ = 5 : 2) gave compound **3c** as a bright yellow solid (70 mg, 14%). M.p.: 125 °C. IR (diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2921, 2852, 1694, 1654, 1609, 1587, 1524, 1465, 1397, 1349, 1237, 1199, 1101, 943, 872, 818, 785, 761. ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm = 8.64–8.54 (m, 2H), 8.40 (d, *J* = 8.5 Hz, 1H), 7.70–7.65 (m, 2H), 7.43 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 5.22–5.15 (m, 1H), 3.07 (s, 6H, NMe_2), 2.29–2.20 (m, 2H, β-CH_2), 1.88–1.80 (m, 2H, β-CH_2), 1.35–1.18 (m, 16H, 8 × CH_2), 0.82 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm = 165.87, 165.64, 164.79, 164.61, 150.65, 147.29, 132.92, 131.57, 131.08, 130.77, 130.17, 129.28, 127.57, 126.59, 126.53, 112.16, 123.66, 122.95, 121.47, 120.75, 54.53, 40.57, 32.62, 31.93, 29.41, 27.07, 22.57, 14.20. MS (EI, 70 eV): *m*/*z* (%) = 499 (22), 498 (59) [M^+], 318 (10), 317 (43), 316 (100), 315 (19). HRMS (EI) for $C_{33}H_{42}N_2O_2$: calcd: 498.3246; found: 498.3227. EA for $C_{33}H_{42}N_2O_2$: calcd: C 79.48, N 5.62, H 8.49; found: C 79.42, N 5.64, H 8.36. UV/Vis ($CHCl_3$): λ_{max} (ε) = 426.2 nm (17 100). Fluorescence ($CHCl_3$, λ_{exc} = 426.2 nm): λ_{max} = 578.4 nm. Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 426.2 nm, $E_{426.2nm,\ 1cm}$ = 0.114, reference: *N*,*N*′-bis(tridecan-7-yl)perylene-3,4:9,10-tetracarboxylic diimide with Φ = 1.00): Φ = 0.64.

6-(3,4,5-Trimethoxyphenyl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3d)

A Schlenk-flask was charged with 6-bromo-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (361 mg, 0.788 mmol, 1.05 equiv.) and 4,4,5,5-tetramethyl-2-(3,4,5-trimethoxyphenyl)-1,3,2-dioxaborolane (220 mg, 0.750 mmol, 1.0 equiv.). Both compounds were dissolved in toluene (20 mL) under a light argon-stream. K_2CO_3 (2.80 g, 20.0 mmol) was dissolved in a mixture of water (10 mL) and EtOH (2 mL) and added to the Schlenk-flask followed by tetrakis(triphenylphosphine)palladium(0) (43 mg, 0.038 mmol, 5 mol%). The mixture was purged with argon for 30 min and then heated to 80 °C. The reaction mixture was stirred at this temperature for further 17 h. After cooling to room temperature, the organic phase was separated and the aqueous phase was extracted with toluene (3 × 20 mL). Purification by column chromatography (silica, $CHCl_3$) gave compound **3d** as yellow oil (350 mg, 86%). IR (diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2924, 2855, 1698, 1656, 1616, 1586, 1503, 1454, 1415, 1397, 1350, 1322, 1237, 1180, 1126, 1104, 1060, 1006, 928, 912, 860, 842, 831, 785, 760, 725, 702, 678. ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm = 8.69 (br s, 2H), 8.31 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.71 (t, *J* = 7.1 Hz, 1H), 6.70 (s, 2H), 5.24–5.13 (m, 1H, NCH), 3.95 (s, 3H, OMe), 3.89 (s, 6H, OMe), 2.31–2.18 (m, 2H, β-CH_2), 1.90–1.77 (m, 2H, β-CH_2), 1.35–1.16 (m, 16H, 8 × CH_2), 0.81 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm = 165.56, 165.36, 164.50, 164.31, 153.45, 146.60, 138.39, 134.53, 132.35, 131.71, 131.23, 130.94, 130.42, 130.14, 128.94, 127.71, 126.99, 123.66, 122.97, 122.55, 121.84, 107.30, 61.12, 56.42, 54.58, 32.52, 31.87, 29.33, 27.00, 22.67, 14.14. MS (EI, 70 eV): *m*/*z* (%) = 545 (40) [M^+], 365 (16), 364 (76), 363 (100), 348 (19). HRMS (EI) for $C_{34}H_{43}NO_5$: calcd: 545.3141; found: 545.3135. EA for $C_{34}H_{43}NO_5$: calcd: C 74.83, N 2.57, H 7.94; found: C 73.47, N 2.58, H 7.75. UV/Vis ($CHCl_3$): λ_{max} (ε) = 362.2 nm (15 900). Fluorescence ($CHCl_3$, λ_{exc} = 362.2 nm): λ_{max} = 525.1 nm. Fluorescence quantum yield

($CHCl_3$, λ_{exc} = 362.2 nm, $E_{362.2nm,\ 1cm}$ = 0.221, reference: *N*,*N*′-bis(tridecan-7-yl)perylene-3,4:9,10-tetracarboxylic diimide with Φ = 1.00): Φ = 0.65.

6-(2,6-Dibromo-3,4,5-trimethoxyphenyl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3e)

6-(3,4,5-Trimethoxyphenyl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]iso-quinoline-1,3(2*H*)-dione (175 mg, 0.320 mmol) was dissolved in 10 mL of acetonitrile. *N*-Bromosuccinimide (120 mg, 0.670 mmol, 2.1 equiv.) was added at once to the solution and the reaction mixture was stirred at 30 °C for 12 h. The crude mixture was treated with brine solution and extracted with chloroform. The organic phase was dried over $MgSO_4$ and concentrated *in vacuo*. Column chromatography ($CHCl_3$) gave **3e** as colorless oil (155 mg, 69%). IR (diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2925, 2855, 1699, 1658, 1590, 1461, 1397, 1352, 1321, 1237, 1179, 1087, 1008, 986, 935, 909, 861, 784, 763, 729. ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm = 8.68–8.54 (m, 2H), 7.72–7.65 (m, 2H), 7.56 (d, *J* = 7.5 Hz, 1H), 5.22–5.15 (m, 1H, NCH), 4.06 (s, 3H, OMe), 3.98 (s, 6H, OMe), 2.28–2.20 (m, 2H, β-CH_2), 1.88–1.82 (m, 2H, β-CH_2), 1.36–1.20 (m, 16H, 8 × CH_2), 0.82 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm = 165.43, 165.21, 164.36, 164.14, 151.23, 147.87, 144.79, 135.49, 131.82, 131.28, 131.06, 130.51, 129.57, 128.63, 128.56, 127.41, 123.93, 123.93, 123.51, 123.20, 122.78, 114.58, 61.54, 61.28, 54.64, 32.56, 31.86, 29.37, 27.05, 22.73, 14.16. MS (EI, 70 eV) *m*/*z* (%): 703 (25), 701 (13) [M$^+$], 525 (12), 524 (48), 523 (31), 522 (100), 521 (31), 520 (50), 399 (9), 397 (9), 361 (25). HRMS (EI) for $C_{34}H_{41}Br_2NO_5$: calcd: 701.1351; found: 701.1357.

6-(3,4,5-Trimethoxy-2,6-dimethylphenyl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3f)

A dry argon flushed Schlenk-flask was charged with $ZnCl_2$ solution (0.43 mL, 0.43 mmol, 1 M, 2.1 equiv.). MeMgCl (0.14 mL, 0.43 mmol, 3.0 M, 2.1 equiv.) was added dropwise to the solution at 0 °C. Another dry argon flushed Schlenk-flask was charged with 6-(2,6-dibromo-3,4,5-trimethoxyphenyl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (145 mg, 0.200 mmol, 1.0 equiv.), $Pd(OAc)_2$ (3.0 mg, 0.010 mmol, 5 mol%) and *S*-Phos (9.0 mg, 0.020 mmol, 10 mol%) in 1.0 mL of dry THF. After stirring for 10 min, this solution was added dropwise to the freshly prepared MeZnCl solution. The reaction mixture was stirred at 60 °C over night and then quenched with sat. aq. NH_4Cl solution. The crude mixture was extracted with chloroform and concentrated *in vacuo*. Column chromatography (silica, $CHCl_3$) gave **3f** as colorless oil (85.0 mg, 74%). IR (diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2925, 2856, 1700, 1658, 1589, 1456, 1399, 1349, 1320, 1237, 1110, 1081, 862, 785, 764. ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm = 8.67–8.52 (br s, 2H), 7.71 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.65–7.59 (m, 1H), 7.51 (d, *J* = 7.4 Hz, 1H), 5.25–5.13 (m, 1H, NCH), 4.02 (s, 3H, OMe), 3.89 (s, 6H, OMe), 2.30–2.20 (m, 2H, β-CH_2), 1.90–1.80 (m, 2H, β-CH_2), 1.75 (s, 6H, 2 × CH_3), 1.35–1.19 (m, 16H, 8 × CH_2), 0.81 (t, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm = 165.58, 164.47, 150.13, 146.23, 145.44, 133.80, 131.68, 131.56, 130.97, 130.79, 130.50, 128.81, 128.22, 127.19, 125.85, 123.88, 123.14, 122.64, 121.90, 60.93, 60.86, 54.59, 32.58, 31.89, 29.39, 27.05, 22.74, 14.16, 13.50. MS (EI, 70 eV) *m*/*z* (%): 574 (18), 573 (43) [M$^+$], 393 (24), 392 (100), 391 (92), 348 (7), 55 (8). HRMS (EI) for $C_{36}H_{47}NO_5$: calcd: 573.3454; found: 573.3448. UV/Vis ($CHCl_3$): λ_{max} (ε) = 358.2 (14 300), 344.0 nm (16 000). Fluorescence ($CHCl_3$, λ_{exc} = 344.0 nm): λ_{max} = 541.6 nm. Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 344.0 nm, $E_{344.0nm,\ 1cm}$ = 0.094, reference: *N*,*N*′-bis(tridecan-7-yl)perylene-3,4:9,10-tetracarboxylic diimide with Φ = 1.00): Φ = 0.046.

6-(4-Methoxynaphthalen-1-yl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3g)

A Schlenk-flask was charged with 6-bromo-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (348 mg, 0.760 mmol, 1.08 equiv.) and 2-(4-methoxynaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (200 mg, 0.700 mmol, 1.0 equiv.). Both compounds were dissolved in toluene (10 mL) under a light argon-stream. K_2CO_3 (1.40 g, 10.0 mmol) was dissolved in a mixture of water (5 mL) and EtOH (1.0 mL) and added to the Schlenk-flask followed by tetrakis-(triphenylphosphine)palladium(0) (20 mg, 0.018 mmol, 5 mol%). The mixture was purged with argon for 30 min and then heated to 80 °C. The reaction mixture was stirred at this temperature for further 17 h. After cooling to room temperature, the organic phase was separated and the aqueous phase was extracted with toluene (3 × 20 mL). Purification by column chromatography (silica, iso-hexane/$CHCl_3$ = 1 : 1) gave compound **3g** as a bright yellow solid (260 mg, 69%). M.p.: 98 °C. IR (diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2920, 2853, 1697, 1655, 1615, 1586, 1511, 1459, 1421, 1398, 1348, 1311, 1235, 1177, 1157, 1106, 1084, 1025, 881, 817, 784, 759, 735, 712, 667. ^{1}H NMR ($CDCl_3$, 300 MHz): δ/ppm = 8.74–8.64 (br s, 1H), 8.64–8.52 (br s, 1H), 8.41 (d, *J* = 8.5 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 1H), 7.57–7.46 (m, 2H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.36–7.27 (m, 2H), 6.97 (d, *J* = 7.9 Hz, 1H) 5.32–5.17 (m, 1H, NCH), 4.11 (s, 3H, OMe), 2.39–2.22 (m, 2H, β-CH_2), 1.96–1.81 (m, 2H, β-CH_2), 1.47–1.15 (m, 16H, 8 × CH_2), 0.85 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ/ppm = 165.51, 164.62, 156.09, 145.53, 133.30, 132.85, 131.64, 131.24, 130.92, 130.50, 129.36, 128.74, 128.69, 128.13, 127.13, 126.82, 125.79, 125.68, 125.61, 122.52, 103.39, 55.80, 54.60, 32.61, 31.92, 29.40, 27.07, 22.74, 14.18. MS (EI, 70 eV) *m*/*z* (%): 535 (32) [M$^+$], 355 (16), 354 (69), 353 (100), 239 (8). HRMS (EI) for $C_{36}H_{41}NO_3$: calcd: 535.3086; found: 535.3080. EA for $C_{36}H_{41}NO_3$: calcd: C 80.71, N 2.61, H 7.71; found: C 80.86, N 2.49, H 7.84. UV/Vis ($CHCl_3$): λ_{max} (ε) = 325.0 nm (15 300). Fluorescence ($CHCl_3$, λ_{exc} = 325.0 nm): λ_{max} = 509.7 nm. Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 325.0 nm, $E_{325.0nm,\ 1cm}$ = 0.139, reference: *N*,*N*′-bis(tridecan-7-yl)perylene-3,4:9,10-tetracarboxylic diimide with Φ = 1.00): Φ = 0.39.

6-(4-Methoxy-8-methylnaphthalen-1-yl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3h)

A Schlenk-flask was charged with 6-bromo-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (124 mg, 0.273 mmol, 1.05 equiv.) and 2-(4-methoxy-8-methylnaphthalen-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (77 mg, 0.26 mmol, 1.0 equiv.). Both compounds were dissolved in toluene (5 mL) under a

light argon-stream. K_2CO_3 (0.700 g, 5.07 mmol) was dissolved in a mixture of water (3 mL) and EtOH (0.5 mL) and added to the Schlenk-flask followed by tetrakis-(triphenylphosphine)palladium(0) (15 mg, 0.013 mmol, 5 mol%). The mixture was purged with argon for 30 min and then heated to 80 °C. The reaction mixture was stirred at this temperature for further 17 h. After cooling to room temperature, the organic phase was separated and the aqueous phase was extracted with toluene (3 × 5 mL). Purification by column chromatography (silica, iso-hexane/$CHCl_3$ = 1 : 1) gave compound **3h** as a bright yellow solid (36.0 mg, 25%). M.p.: 164 °C. IR (diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2920, 2853, 1697, 1656, 1587, 1513, 1450, 1397, 1344, 1314, 1233, 1153, 1099, 1045, 815, 784, 765, 726, 677. ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm = 8.66–8.50 (br, 2H), 8.38 (d, J = 7.9 Hz, 1H), 7.76 (dd, J = 8.4, 1.1 Hz, 1H), 7.70 (d, J = 7.4 Hz, 1H), 7.57–7.53 (m, 1H), 7.45–7.41 (m, 1H), 7.24 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 8.0 Hz, 1H), 5.24–5.17 (m, 1H, NCH), 4.09 (s, 3H, OMe), 2.30–2.21 (m, 2H, β-CH_2), 1.92–1.82 (m, 2H, β-CH_2), 1.74 (s, 3H, CH_3), 1.36–1.20 (m, 16H, 8 × CH_2), 0.84 (t, J = 6.5 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm = 165.62, 164.67, 156.42, 149.90, 134.47, 132.86, 132.51, 132.22, 131.60, 130.85, 130.12, 128.70, 128.26, 127.00, 126.83, 125.54, 123.58, 122.88, 122.36, 121.64, 121.23, 102.85, 55.91, 54.67, 32.57, 31.93, 29.43, 27.14, 24.58, 22.78, 14.22. MS (EI, 70 eV) m/z (%): 550 (22), 549 (50) [M^+], 380 (6), 369 (13), 368 (62), 367 (100), 352 (8), 309 (5). HRMS (EI) for $C_{37}H_{43}NO_3$: calcd: 549.3243; found: 549.3238. EA for $C_{37}H_{43}NO_3$: calcd: C 80.84, N 2.55, H 7.88; found: C 80.32, N 2.54, H 8.00. UV/Vis ($CHCl_3$): λ_{max} (ε) = 329.0 nm (17 100). Fluorescence ($CHCl_3$, λ_{exc} = 329.0 nm): λ_{max} = 522.7 nm. Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 329.0 nm, $E_{329.0nm,\ 1cm}$ = 0.063, reference: *N*,*N*′-bis(tridecan-7-yl)perylene-3,4:9,10-tetracarboxylic diimide with Φ = 1.00): Φ = 0.40.

6-(4-(Trimethylsilyl)phenyl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3i)

A Schlenk-flask was charged with 6-bromo-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (1.33 g, 2.92 mmol, 1.05 equiv.) and (4-(trimethylsilyl)phenyl)boronic acid (540 mg, 2.78 mmol, 1.0 equiv.). Both compounds were dissolved in toluene (40 mL) under a light argon-stream. K_2CO_3 (8.40 g, 60.0 mmol) was dissolved in a mixture of water (30 mL) and EtOH (5.00 mL) and added to the Schlenk-flask followed by tetrakis(triphenylphosphine)palladium(0) (160 mg, 0.140 mmol, 5 mol%). The mixture was purged with argon for 30 min and then heated to 80 °C. The reaction mixture was stirred at this temperature for further 17 h. After cooling to room temperature, the organic phase was separated and the aqueous phase was extracted with toluene (3 × 30 mL). Purification by column chromatography (silica, iso-hexane/$CHCl_3$ = 1 : 1) gave compound **3i** as green fluorescent oil (1.19 g, 81%). IR (diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2923, 2855, 1698, 1656, 1587, 1455, 1398, 1349, 1237, 1179, 1111, 838, 820, 784, 761, 726, 695. ^{1}H NMR ($CDCl_3$, 400 MHz): δ/ppm = 8.71–8.56 (br s, 2H), 8.30 (dd, J = 8.5, 1.1 Hz, 1H), 7.71 (dd, J = 7.9, 2.6 Hz, 3H), 7.51 (d, J = 8.1 Hz, 1H), 5.28–5.16 (m, 1H, NCH), 2.35–2.22 (m, 2H, β-CH_2), 1.93–1.79 (m, 2H, β-CH_2), 1.46–1.14 (m, 16H, 8 × CH_2), 0.83 (t, J = 6.9 Hz, 6H), 0.36 (s, 9H, TMS). ^{13}C NMR ($CDCl_3$, 100 MHz): δ/ppm = 165.63, 165.46, 164.58, 164.39, 146.65, 141.05, 139.33, 133.72, 132.44, 131.67, 131.34, 130.89, 130.58, 130.04, 129.29, 129.02, 127.91, 126.91, 123.71, 123.02, 122.58, 121.84, 54.58, 32.57, 31.90, 29.37, 27.04, 22.71, 14.17, −0.97. MS (EI, 70 eV) m/z (%): 527 (20) [M^+], 348 (8), 347 (29), 346 (100), 345 (26), 331 (11), 330 (33). HRMS (EI) for $C_{34}H_{45}NO_2Si$: calcd: 527.3220; found: 535.3216. EA for $C_{34}H_{45}NO_2Si$: calcd: C 77.37, N 2.65, H 8.59; found: C 77.02, N 2.73, H 8.63. UV/Vis ($CHCl_3$): λ_{max} (ε) = 356.0 nm (18 600). Fluorescence ($CHCl_3$, λ_{exc} = 356.0 nm): λ_{max} = 425.4 nm. Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 356.0 nm, $E_{356.0nm,\ 1cm}$ = 0.068, reference: *N*,*N*′-bis(tridecan-7-yl)perylene-3,4:9,10-tetracarboxylic diimide with Φ = 1.00): Φ = 0.79.

6-(4-Cyanophenyl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3j)

Procedure A: Suzuki-coupling. A Schlenk-flask was charged with 6-bromo-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (980 mg, 2.10 mmol, 1.0 equiv.) and 4-cyanophenylboronic acid (970 mg, 2.52 mmol, 1.2 equiv.). Both compounds were dissolved in toluene (40 mL) under a light argon stream. K_2CO_3 (5.00 g, 36.2 mmol) was dissolved in a mixture of water (20 mL) and EtOH (8 mL) and added to the Schlenk-flask followed by tetrakis-(triphenylphosphine)palladium(0) (115 mg, 0.110 mmol, 5.00 mol%). The mixture was purged with argon for 30 min and then heated to 80 °C. The reaction mixture was stirred at this temperature for further 17 h. After cooling to room temperature, the organic phase was separated and the aqueous phase was extracted with toluene (3 × 20 mL). Purification by column chromatography (silica, iso-hexane/$CHCl_3$ = 1 : 1) gave compound **3j** as bright yellow oil (416 mg, 41%).

Procedure B: cyanation with $K_4Fe(CN)_6$. A dry argon flushed Schlenk-flask was charged with potassium hexacyanidoferrate(II) ($K_4Fe(CN)_6$, 128 mg, 0.348 mmol, 2.0 equiv.), potassium carbonate (K_2CO_3, 72.1 mg, 0.522 mmol, 3.0 equiv.) and [1,1′-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (Pd(dppf)Cl_2, 12.7 mg, 0.0174 mmol, 10 mol%). A solution of 6-(4-iodophenyl)-2-(tridecan-7-yl)-1*H*-benzo-[*de*]isoquinoline-1,3(2*H*)-dione (101 mg, 0.174 mmol) in 1.7 mL of dry *N*,*N*-dimethylformamide was added at room temperature under argon. The reaction mixture was stirred at 100 °C for 4 h, allowed to cool down and the solvent was removed under reduced pressure. The crude residue was treated with 15 mL of sat. aq. NH_4Cl solution and extracted with chloroform (3 × 15 mL). Purification by column chromatography (silica, iso-hexane/$CHCl_3$ = 1 : 1) gave compound **3j** as bright yellow oil (54.9 mg, 0.114 mmol, 66%). IR (diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2923, 2855, 1699, 1656, 1588, 1465, 1397, 1349, 1327, 1238, 1179, 1103, 844, 784, 759. ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm = 8.71–8.60 (br s, 2H), 8.36 (dd, J = 8.5 Hz, 1.0 Hz, 1H), 7.89 (d, J = 8.4 Hz, 2H), 7.78 (d, J = 7.5 Hz, 1H), 7.77–7.73 (m, 1H), 7.67 (d, J = 8.4 Hz, 2H), 5.23–5.18 (m, 1H, NCH), 2.30–2.23 (m, 2H, β-CH_2), 1.89–1.82 (m, 2H, β-CH_2), 1.37–1.20 (m, 16H, 8 × CH_2), 0.84 (t, J = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm = 165.67, 165.49, 164.58, 164.41, 146.08, 140.64, 138.49, 132.32, 131.81, 131.40, 131.02, 130.70, 130.08, 129.10, 128.02, 127.56,

127.12, 123.83, 123.10, 122.77, 122.05, 54.70, 32.60, 31.94, 29.41, 27.09, 22.76, 14.21. MS (EI, 70 eV) *m*/*z* (%): 480 (2) [M^+], 299 (17). HRMS (EI) for $C_{32}H_{36}N_2O_2$: calcd: 480.2777; found: 480.2773. UV/Vis ($CHCl_3$): λ_{max} (ε) = 366.4 nm (23 700). Fluorescence ($CHCl_3$, λ_{exc} = 366.4 nm): λ_{max} = 447.4 nm. Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 366.4 nm, $E_{366.4nm,\ 1cm}$ = 0.073, reference *N*,*N*′-bis(tridecan-7-yl)perylene-3,4:9,10-tetracarboxylic diimide with Φ = 1.00): Φ = 0.54.

6-(4-Iodophenyl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3k)

A dry, argon flushed Schlenk-flask was charged with 6-(4-(trimethylsilyl)phenyl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]iso-quinoline-1,3(2*H*)-dione (840 mg, 1.60 mmol, 1.0 equiv.) and dry dichloromethane (3.5 mL). The flask was cooled to 0 °C and iodine monochloride (260 mg, 1.60 mmol, 1.0 equiv.) was added dropwise to the mixture. After stirring at 0 °C for 10 min, the reaction mixture was quenched with sat. aq. $Na_2S_2O_3$ solution (5 mL), extracted with dichloromethane (3 × 10 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography (silica, $CHCl_3$) to obtain **3k** as yellow oil (770 mg, 83%). IR (diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2922, 2854, 1698, 1656, 1588, 1487, 1463, 1398, 1349, 1324, 1238, 1178, 1101, 1005, 821, 784, 758. ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm = 8.65–8.56 (m, 2H), 8.18 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.70–7.66 (m, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 5.22–5.15 (m, 1H, NCH), 2.27–2.20 (m, 2H, β-CH_2), 1.86–1.79 (m, 2H, β-CH_2), 1.32–1.15 (m, 16H, 8 × CH_2), 0.79 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm = 165.41, 165.22, 164.35, 164.13, 145.17, 138.40, 137.92, 133.52, 131.82, 131.65, 131.19, 130.97, 130.44, 129.71, 128.92, 127.76, 127.15, 126.97, 123.74, 123.03, 122.87, 122.19, 94.61, 54.57, 32.48, 31.84, 29.30, 26.98, 22.65, 14.13. MS (EI, 70 eV) *m*/*z* (%): 581 (11) [M^+], 401 (12), 400 (68), 399 (16), 199 (12), 198 (100). HRMS (EI) for $C_{31}H_{36}INO_2$: calcd: 581.1791; found: 581.1781. EA for $C_{31}H_{36}INO_2$: calcd: C 64.03, N 2.41, H 6.24; found: C 63.88, N 2.49, H 6.32.

6-(4′-Methoxy-[1,1′-biphenyl]-4-yl)-2-(tridecan-7-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione (3l)

A dry argon flushed Schlenk-flask was charged with 4-iodoanisole (40.0 mg, 0.16 mmol, 1.0 equiv.) and dry THF (1.00 mL). An iodine/magnesium exchange was performed using iPrMgCl·LiCl (0.13 mL, 0.16 mmol, 1.26 M, 1.0 equiv.) within 20 min at 0 °C, followed by transmetalation with $ZnCl_2$ (0.18 mL, 0.18 mmol, 1.00 M, 1.1 equiv.). The freshly prepared zinc species was transferred *via* a syringe to another argon flushed Schlenk-flask which was previously charged with 6-(4-iodophenyl)-2-(tridecan-7-yl)-1*H*-benzo-[*de*]isoquinoline-1,3-(2*H*)-dione (96.0 mg, 0.16 mmol, 1.0 equiv.), palladium(0)bis-(dibenzylideneacetone) (5 mg, 0.008 mmol, 5 mol%), tris-(2-furyl)phosphine (4.0 mg, 0.016 mmol, 10 mol%) and dry THF (3 mL). The reaction mixture was stirred at 50 °C for 12 h, quenched with sat. aq. NH_4Cl solution, extracted with dichloromethane (3 × 5 mL) and dried over $MgSO_4$. After filtration, the solvents were evaporated *in vacuo*. The crude product was purified by flash column chromatography (silica, iso-hexane/dichloromethane = 1 : 1) to obtain **3l** as a yellow solid (80.0 mg, 89%). M.p.: 104 °C. IR (diamond-ATR, neat): $\tilde{\nu}$/cm^{-1} = 2924, 2854, 1697, 1652, 1604, 1587, 1497, 1464, 1396, 1349, 1288, 1238, 1177, 1106, 1039, 823, 784, 760. ^{1}H NMR ($CDCl_3$, 600 MHz): δ/ppm = 8.70–8.56 (m, 2H), 8.35 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.76–7.73 (m, 3H), 7.73–7.69 (m, 1H), 7.64 (d, *J* = 8.9 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.8 Hz, 2H), 5.23 (m, 1H, NCH), 7.04 (s, 3H, OMe), 2.31–2.21 (m, 2H, β-CH_2), 1.89–1.80 (m, 2H, β-CH_2), 1.36–1.20 (m, 16H, 8 × CH_2), 0.83 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz): δ/ppm = 165.70, 164.46, 159.69, 146.41, 141.13, 137.31, 132.94, 132.47, 131.74, 131.41, 130.96, 130.63, 130.48, 130.11, 129.08, 128.34, 127.95, 127.04, 127.00, 123.76, 123.04, 122.54, 121.82, 114.57, 55.55, 54.65, 32.60, 31.93, 29.41, 27.08, 22.75, 14.21. MS (EI, 70 eV) *m*/*z* (%): 562 (11), 561 (25) [M^+], 392 (7), 381 (20), 380 (76), 379 (100), 364 (7), 336 (7). HRMS (EI) for $C_{38}H_{43}NO_3$: calcd: 561.3243; found: 561. 3229. EA for $C_{38}H_{43}NO_3$: calcd: C 81.25, N 2.49, H 7.72; found: C 81.37, N 2.49, H 7.76. UV/Vis ($CHCl_3$): λ_{max} (ε) = 364.4 nm (27 500). Fluorescence ($CHCl_3$, λ_{exc} = 364.4 nm): λ_{max} = 492.2 nm. Fluorescence quantum yield ($CHCl_3$, λ_{exc} = 364.4 nm, $E_{364.4nm,\ 1cm}$ = 0.053, reference: *N*,*N*′-bis(tridecan-7-yl)perylene-3,4:9,10-tetracarboxylic diimide with Φ = 1.00): Φ = 0.67.

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