Tailored Synthesis of *N*-Substituted *peri*-Xanthenoxanthene Diimide (PXXDI) and Monoimide (PXXMI) Scaffolds

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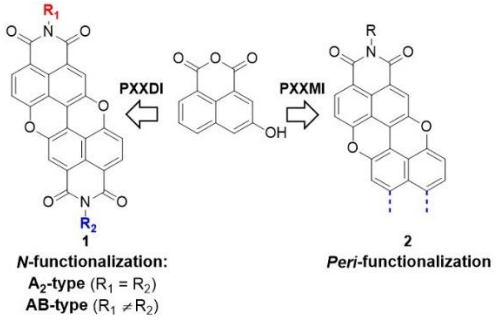


ABSTRACT: The tailored synthesis of homo (A_2) and hetero (AB) *N*-substituted *peri*-xanthenoxanthene diimides (PXXDIs) and *peri*-functionalized PXX monoimides (PXXMIs) from 3-hydroxy naphthalic anhydride is described. As A_2-type PXXDIs could be synthesized in one step, AB-type PXXDIs and PXXMIs were prepared through a modular approach capitalizing on sequential *Suzuki* coupling, Imidation and *Pummerer* reactions with very high yields. In view of their potential applications as organic semiconductors, self-organization studies were performed through liquid deposition on surfaces, depicting the formation of islands, needles and rods.

INTRODUCTION

O-doped polycyclic aromatic hydrocarbons are attracting significant attention as materials for opto-electronic applications.[1] Among the different families, *peri*-xanthenoxanthene (PXX)[2] have firstly debuted as *p*-type organic semiconductors to engineer flexible OLEDs.[3] The re-emergence of such interesting PXX-based chromophores recently engendered synthetic programs in our and other laboratories.[4] Our group has expanded the structural diversity of PXX and developed a variant of the oxidative *Pummerer* O-annulation reaction to prepare *peri*-substituted PXXs featuring ribbon-like structures with either armchair[5] or zig-zag[6] peripheries and π-extended surfaces.[7] Very recently, we prepared the first mimics of naphthalene-diimide (NDI),[8] perylene-monoimide (PMI) and -diimide (PDI) molecules,[9] in which the PXX core exposes either one (PXXMI) or two (PXXDI) alkylimide groups (Figure 1).[10] *N*-octyl PXXMI and PXXDI display good solubility in organic solvents, green-centered UV-vis absorption, high emissive quantum yields (Φ = 40 - 70%, τ = 3 - 9 ns), and HOMO and LUMO levels rigidly shifted at higher energies than those measured for PDI derivatives.[10] In contrast to PDIs, both PXXMIs and PXXDIs can act as *p*-type semiconductors.

Current synthetic route (Figure 1) gives access to A_2-type *N*-substituted PXXDIs,[10] and it involves subsequent imidation, *Suzuki* C-C coupling, and O-annulation reactions (Imidation-*Suzuki*-*Pummerer* strategy, ISP) as the crucial steps.[10] Nevertheless, the lack of a simple protocol providing access to any *N*-substituted derivatives and of a synthetic plan giving AB-type PXXDIs limits the applicability of the current pathway. It is considering these drawbacks that herein we report new high-yielding synthetic paths for preparing A_2- and AB-type PXXDIs as well as PXXMIs.

As one can easily anticipate, the divergent chemical transformation limiting the scope of the current synthetic route is the imidation reaction. Thus, a decision was made to install the imidic group fairly late in the synthesis (Figure 1). In this work we envisage to relegate the imidation step at the penultimate step of the synthetic plan and use either a direct oxidative *Pummerer* dimerization (IP route) to obtain A_2-type derivatives from 3-hydroxy naphthalene imide precursors, or a sequential *Suzuki*-Imidation-*Pummerer* synthetic strategy (SIP) to give both A_2- and AB-type PXXDIs. Capitalizing on the SIP strategy, a variety of *N*-substituted PXXMIs could also be readily prepared, including a blue-colored, NIR-emitting *N*-octyl *peri*-π-extended PXXMI.

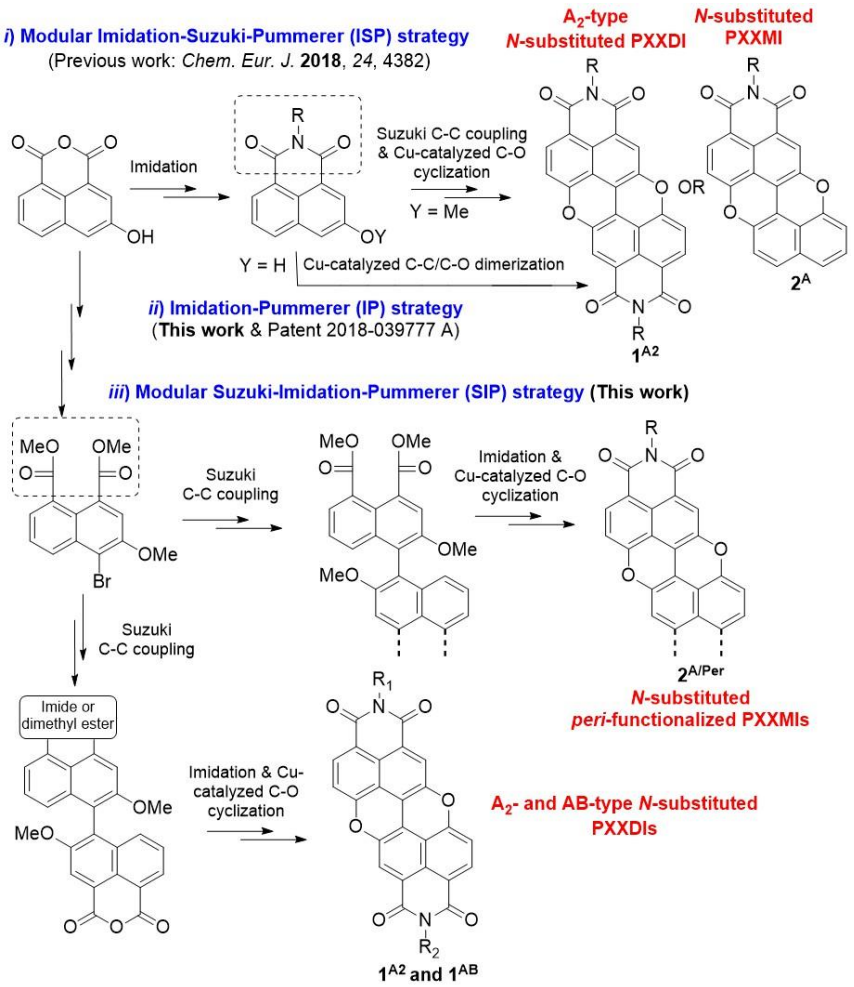
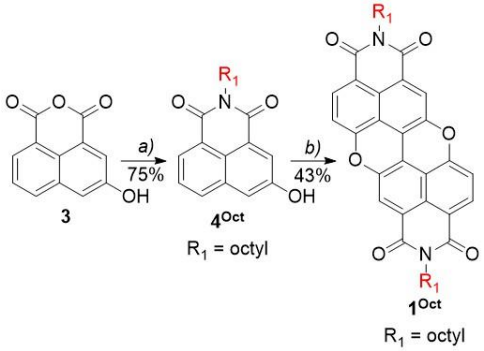


Figure 1. Synthetic strategies toward the preparation of *N*-substituted A_2- ($R_1 = R_2$) and AB-type ($R_1 \neq R_2$) PXXDIs and *peri*-π-extended PXXMIs.

- RESULTS AND DISCUSSION

Inspired by the protocol of *Bolloweg et al.* to prepare PXX through direct oxidation of naphthol with CuO,[11] our investigations debuted with a homocoupling procedure (IP strategy, Figure 1) to afford A_2-type PXXDIs from the relevant *N*-substituted 3-hydroxy-naphthalene imide precursor.

Scheme 1. Synthesis of *N*-substituted A_2-type PXXDIs[a]

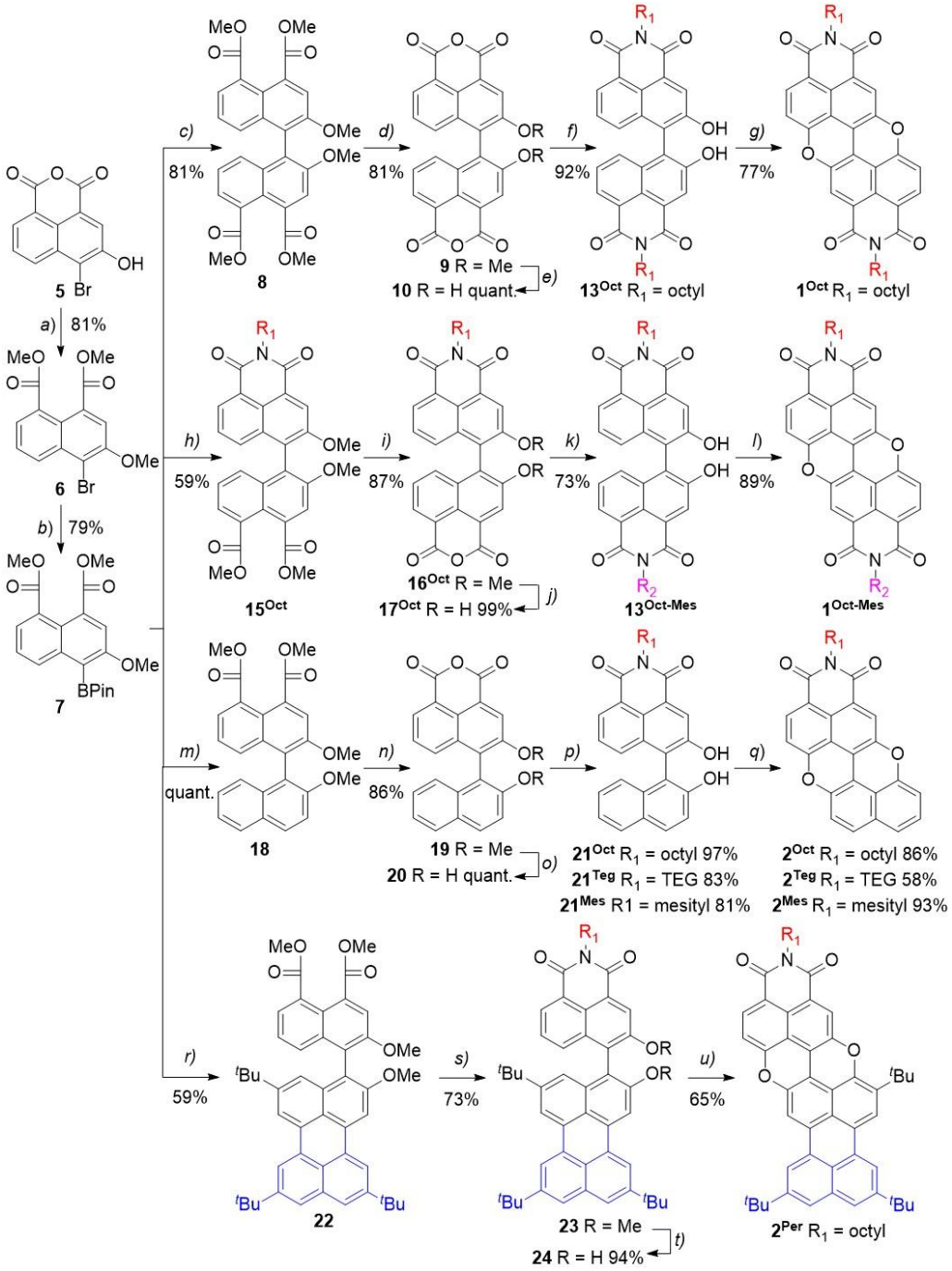


[a]Imidation-*Pummerer* strategy. Reagents and conditions: a) *n*-octylamine, DIPEA, 1,4-dioxane, reflux, 16 h; b) CuCl, DMSO, 120 °C, 24 h, air (43%) or CuI, PivOH, DMSO 150 °C, 5 h, air (20%).

As the model reagent, we prepared naphthalene imide $\mathbf{4}^{Oct}$ (Scheme 1). Our studies commenced by examining the homocoupling method using CuO in refluxing $PhNO_2$, which gave $\mathbf{1}^{Oct}$ in 13% yield. When using CuI and PivOH in DMSO at 150 °C for 5 h in air,[5-7,10] we improved the yield to 20%. Simultaneously to our investigations, a related work by *Kamei et al.* describing the high-yielding synthesis of A_2-type PXXDIs following the IP strategy using CuCl in DMSO at 120 °C appeared as a patent.[12] In our hands, *Kamei et al.* conditions gave $\mathbf{1}^{Oct}$ in 43% isolated yield.

Anticipating a potential susceptibility of the *N*-substituent with the oxidative protocol of the IP strategy, we developed a route in which the O-annulation is performed with a binaphthol precursor with shorter times (Scheme 2). In this synthetic plan, the imidation reaction is relegated to the second to last step. Bromination[10] of 3-hydroxy-1,8-naphthalic anhydride **3** with Br_2 (Scheme S2) followed by alkylation with MeI in the presence of DBU in MeOH[13] gave dimethyl ester **6** in 81% yield that, coupled to its boronic-ester derivative **7** through *Suzuki* reaction, gave tetramethyl ester **8** in 81% yield. Subsequent saponification of **8** with KOH in *i*PrOH followed by addition of $HCl_{(aq.)}$ in AcOH gave bisanhydride **9** in 81% yield.

Scheme 2. Synthesis of *N*-substituted A_2- and AB-type PXXDIs, PXXMIs and *peri*-π-extended PXXMI[a]



[a]*Suzuki*-Imidation-*Pummerer* strategy. Reagents and conditions: a) DBU, MeI, MeOH, reflux, 18 h; b) B_2Pin_2, KOAc, $[Pd(PPh_3)_2Cl_2]$, 1,4-dioxane, reflux, 16 h; c, h, m, r) **6** or $\mathbf{14}^{Oct}$ or **27** or **28**, K_3PO_4, $[Pd(dba)_2]$, SPhos, 1,4-dioxane, H_2O, reflux, 16-24 h; d, n) 1. KOH, *i*PrOH, reflux, 13 h; 2. $HCl_{(aq.)}$, AcOH, reflux, 24 h; e) $HBr_{(aq.)}$, AcOH, 126 °C, 24 h; f) *n*-octylamine, DIPEA, 1,4-dioxane, reflux, 24 h; g) CuCl, DMSO, 120 °C, 24 h, air (41%) or CuI, PivOH, DMSO, 120 °C, 5 h, air (77%); i) TFA, reflux, 24 h; j, o) BBr_3 (1M in CH_2Cl_2), CH_2Cl_2, 0 °C to r.t., 12-16 h; k) 2,4,6-trimethylaniline, imidazole, 150 °C, 12 h; l, q, u) CuI, PivOH, DMSO, 120-150 °C, 3-5 h, air; p) *n*-octylamine, DIPEA, 1,4-dioxane, reflux, 20 h or 2,4,6-trimethylaniline, imidazole, 130 °C, 3 h, N_2 or 2-(2-(2-aminoethoxy)ethoxy)ethan-1-ol, DIPEA, 1,4-dioxane, reflux, 20 h; s) 1. KOH, *i*PrOH, reflux 12 h, 2. $HCl_{(aq.)}$, 3. *n*-octylamine, DIPEA, 1,4-dioxane, reflux, 20 h; t) $CH_3(CH_2)_9SH$, NaOH, NMP, 130 °C, 4 h.

Cleavage of the methoxy groups with HBr in AcOH[14] and condensation reaction with *n*-octylamine afforded binaphthol diimide $\mathbf{13}^{Oct}$ in 92% yield. Final C-O cyclization using Cu(I) salt, PivOH in DMSO under open air conditions gave final PXXDI $\mathbf{1}^{Oct}$ in 77% yield as previously reported.[10] Notably, when the O-annulation was performed without PivOH acid, the yield decreased to 41%. Having a considerable quantity of bisnaphthalene

anhydride **10** in hand, one can envisage to construct a wide series of A_2-type *N*-substituted binaphthol diimides using the relevant amines and cyclize them into PXXDIs. Considering that the IP route would potentially yield to mixtures of *N*-substituted PXXDIs (the A_2-, AB- and B_2-type derivatives), we turned our gaze to the SIP route for tailoring AB-type PXXDIs (Scheme 1).

Building on the strategy developed to prepared AB-type *N*-substituted NDIs,[15] we first inferred that sequential condensation reactions, involving mono anhydride intermediates, could give access to AB-type PXXDIs starting from tetramethyl ester **8** (Scheme S4). Thus, we decided to undertake the preparation of a mono anhydride derivative by acid hydrolysis of **8** using several acids such as *p*TosOH · H_2O, $HCl_{(aq.)}$ and TFA in different solvents (*e.g.*, toluene, hexane and $CHCl_3$). Unfortunately, none of the tested reaction conditions gave the monoanhydride, and only an inseparable mixture of mono and dianhydride derivatives was obtained. Therefore, we focused on the Pd-catalyzed C-C bond formation as the hetero-coupling reaction (Scheme 2). *Suzuki* cross-coupling between *N*-functionalized Br-derived naphthalene imide $\mathbf{14}^{Oct}$[10] and boronic pinacol ester **7** gave dimethyl ester-monoimide $\mathbf{15}^{Oct}$ in 59% yield. Subsequent anhydride formation in TFA followed by the deprotection of the methoxy groups and imidation reaction with 2,4,6-trimethylaniline at 150 °C, gave AB-type *N*-substituted diimide $\mathbf{13}^{Oct\text{-}Mes}$ in 63% over three steps. Final *Pummerer* O-annulation gave targeted AB-type PXXDI $\mathbf{1}^{Oct\text{-}Mes}$ in 89% yield.

At last, we prepared *peri*-functionalized PXXMIs following the SIP route (Schemes 1, S5-S6). As anticipated for the A_2-type PXXDIs, intermediate **7** can be also regarded as the crucial substrate for the synthesis of PXXMIs. In fact, *Suzuki* cross-coupling of boronic acid **7** with the relevant aryl bromide (*i.e.*, naphthalene **27** or perylene **28**) in the presence of $[Pd(dba)_2]$ and SPhos afforded bi-aryl compounds **18** and **22** in quantitative and 59% yield, respectively. Alkaline hydrolysis followed by acidic-catalyzed cyclization gave the anhydride intermediates in high yields. In the case of **22**, subsequent imidation reaction with *n*-octylamine and deprotection of methoxy groups using 1-decanethiol (NaOH in NMP) gave targeted monoimide derivative **24**. On the other hand, removal of the methoxy groups in anhydride **18** with BBr_3 gave intermediate **20** that was transformed into the given binaphthyl imide derivative ($\mathbf{21}^{Oct/Teg/Mes}$) by imidation reaction using the relevant amine. O-annulation of dihydroxy intermediates $\mathbf{21}^{Oct/Teg/Mes}$ and **24** using CuI and PivOH in DMSO at 120-150 °C yielded targeted PXXMIs $\mathbf{2}^{Oct/Teg/Mes}$ (58%-93%) and $\mathbf{2}^{Per}$ (65%). All intermediates and final products were unambiguously identified by ^{1}H- and ^{13}C-NMR spectroscopy and HR-MS spectrometry.

The photophysical studies of PXXDIs and PXXMIs were performed in CH_2Cl_2 solutions by steady-state UV/Vis absorption and emission spectroscopy (Table 1). The absorption spectra of A_2- and AB-type *N*-substituted PXXDIs show the characteristic features of imide-functionalized PAHs[10] with an absorption maximum

Table 1. Photophysical data in aerated CH_2Cl_2 at r.t.

	Absorption		Emission		Stokes shift (nm)	Optical gap (eV)[d]
	λ_{max} (nm)[b]	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_F (%)		
$\mathbf{1}^{Oct}$ [a]	538	43500	548	39%	10	2.28
$\mathbf{1}^{Oct\text{-}Mes}$	540	50600	549	49%	9	2.27
$\mathbf{2}^{Oct}$ [a]	525	17800	564	68%	39	2.28
$\mathbf{2}^{Teg}$	528	17800	568	73%	40	2.27
$\mathbf{2}^{Mes}$	529	18200	567	74%	38	2.27
$\mathbf{2}^{Per}$	628	23100	710	3%[c]	82	1.86

[a] Data taken from reference (10). [b] Standard: Rhodamine 6G in EtOH (Φ = 0.94).[16] [c] Standard: coumarine 153 in EtOH (Φ = 0.53).[16] [d] The optical gap is calculated using the intersection wavelength between the respective normalized absorption and emission spectra (λ_{int}) following the formula: Optical gap = $1240/\lambda_{int}$ (eV)

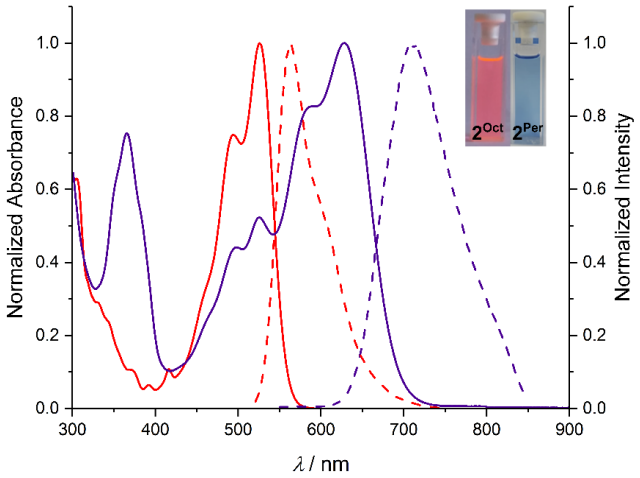


Figure 2. Absorption (—) and emission (---) spectra of $\mathbf{2}^{Oct}$ (red, λ_{exc} = 520 nm) and $\mathbf{2}^{Per}$ (blue, λ_{exc} = 497 nm) in aerated CH_2Cl_2 at r.t.

centered at 538 nm (ε = 43500 M^{-1} cm^{-1}) and 540 nm (ε = 50600 M^{-1} cm^{-1}) for $\mathbf{1}^{Oct}$ and $\mathbf{1}^{Oct\text{-}Mes}$, respectively. As expected, the *N*-substitution has a small effect on the UV-vis absorption properties, caused by the desymmetrization of the PXXDI and possible aggregation phenomena as described for the perylene bisimide.[17] Similarly, the emission profiles and fluorescence quantum yields are negligibly influenced by the chemical nature of the *N*-substituent (Figure S54). Analogously, the PXXMIs bearing different *N*-substituents depict very similar absorption profiles with a maximum band at 525, 528 and 529 nm for $\mathbf{2}^{Oct}$, $\mathbf{2}^{Teg}$ and $\mathbf{2}^{Mes}$ respectively (Figures 2 and S55). Alike to PXXDIs, the luminescence spectra of both $\mathbf{2}^{Teg}$ and $\mathbf{2}^{Mes}$ display equivalent emission profiles with high fluorescence quantum yields (Φ ~ 70%) to that of $\mathbf{2}^{Oct}$ (Φ = 68%). The effect of the *peri*-fusion of a naphthalene unit in PXXMI $\mathbf{2}^{Per}$ causes a strong red-shift of the UV-vis absorption profile when compared to that of $\mathbf{2}^{Oct}$, displaying the lowest-energy transition at 628 nm (ε = 23100 M^{-1} cm^{-1}). PXXMI $\mathbf{2}^{Per}$ exhibits a red emission centered at 710 nm (Φ

= 3% and 10% in aerated CH_2Cl_2 and toluene, respectively). While the solvent seems to have a negligible effect on the UV-Vis absorption, a bathochromic shift of the emission peak has been observed upon increasing the solvent polarity (Figures S56-S57). Likely, this effect can be attributed to an intramolecular charge transfer character of the lowest-energy transition (*i.e.*, from the O-doped electron donating perylene π-scaffolding to the electron-depleting imide group). It is noteworthy to indicate that the chemical nature of *N*-substituents has a small effect on the redox properties of both PXXMI and PXXDI (Table 2). As depicted in the diagram, the *N*-substituents display very similar HOMO and LUMO energy levels, whereas only **2**^{Per} has a significantly lowered LUMO level (Figures 3, S58 and S59).

Table 2. CV data in CH_2Cl_2 at RT[a]

	$E^{1/2}_{ox,1}$ (V) [a]	$E^{1/2}_{red,1}$ (V) [a]	$E^{1/2}_{red,2}$ (V) [a]	E_{HOMO} (eV)[c]	E_{LUMO} (eV) [c]
1^{Oct} [b]	0.95	-1.47	-1.65	-6.05	-3.63
1$^{Oct-Mes}$	0.99	-1.44	-1.64	-6.09	-3.66
2^{Oct} [b]	0.64	-1.77	nd	-5.74	-3.33
2^{Teg}	0.68	-1.72	nd	-5.78	-3.38
2^{Mes}	0.69	-1.73	nd	-5.79	-3.37
2^{Per}	0.74 [d]	nd	nd	-5.84	-3.98 [e]

[a] Halfwave potential in V vs. Fc^+/Fc. [b] Data taken from reference (10). [c] HOMO and LUMO energies are calculated from the respective halfwave potential by assuming that the formal potential of the ferrocene redox couple, taken as a reference, is at -5.1 eV vs. vacuum and following the formulae: $E_{HOMO} = E^{1/2}_{ox,1}$ - 5.1 (eV) and $E_{LUMO} = E^{1/2}_{red,1}$ - 5.1 (eV). [d]Additional peaks were observed while oxidizing, suggesting that an induced aggregation or minor decomposition is probably occurring the CV cycling. [e] Calculated using the optical gap following the formula: $E_{LUMO} = E_{HOMO}$ + optical gap (eV). nd stands for not determined.

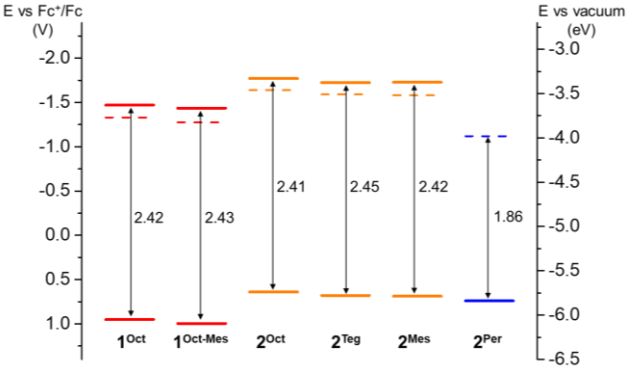


Figure 3. Frontier orbital energies for the PXXMIs and PXXDIs in CH_2Cl_2. Dashed lines correspond to calculated LUMO energies using optical gap in the same solvent using the formula: $E_{LUMO} = E_{HOMO}$ + optical gap (eV). The formal potential of the reference Fc/Fc^+ redox couple is assumed to be at -5.1 eV vs. vacuum.

As solution processability represents one of the hallmarks for preparing nanostructured materials to be used as organic semiconductors, we studied the self-organization properties of **1**^{Oct}, **2**^{Oct} and **2**^{Per} by AFM imaging of the nanostructures (Figure 4, left) formed on Al_2O_3 surfaces upon spin-coating deposition of a $CHCl_3$ solution (c = 0.25 mg mL^{-1}). While multilayered nanometer-sized leaf-like and needle-like objects for **1**^{Oct} and **2**^{Oct} have been obtained, amorphous aggregates were observed for **2**^{Per}. It is worth to underline that the morphologies constituted by **1**^{Oct} and **2**^{Per} are formed through a typical Volmer-Weber growth mechanism,[18] for

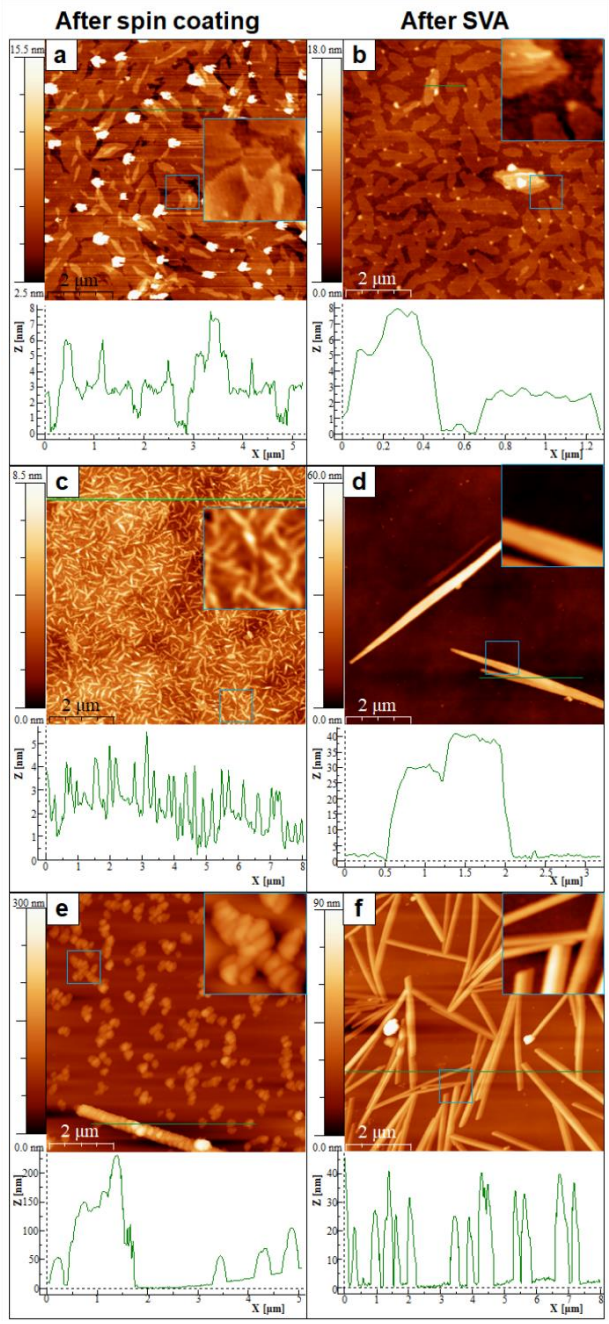


Figure 4. AFM height imaging of **1**^{Oct} (a, b), **2**^{Oct} (c, d) and **2**^{Per} (e, f) on Al_2O_3 before (left) and after 16 h of SVA (right) using $CHCl_3$ at r.t. Deposition achieved through spin-coating of a 0.25 mg/mL $CHCl_3$ solution of the relevant molecule on Al_2O_3.

which the growth is preferred to occur on the soft-matter rather than on the Al_2O_3 substrate. Solvent vapor annealing (SVA) was employed as post-deposition treatment to enhance the crystallinity of the nanostructures as well as their homogeneity.[19] The spin-coated samples were thus exposed to a saturated atmosphere of $CHCl_3$ vapors for 16 h at r.t. (Figure 4, right). For **1**^{Oct}, SVA procedure led to a redistribution of the material to a uniform surface distribution. On the other hands, under SVA conditions PXXMIs **2**^{Oct} and **2**^{Per} reorganize into needles (l < 10 μm, w < 400 nm) and rods (0.25 < l < 4.5 μm, w < 200 nm), respectively.

CONCLUSIONS

In conclusion, we have developed novel syntheses affording highly luminescent and soluble homo and hetero *N*-substituted PXXDIs and *peri*-functionalized PXXMIs. A_2-type PXXDIs can be accessed following either a direct *Pummerer* dimerization or a sequential SIP strategy. Relegating the imidation to a final stage of the synthesis allowed us to also develop a tailored synthetic route to prepare AB-type PXXDIs. The SIP methodology could also be used to readily prepare PXXMIs featuring either different *N*-substituents or *peri*-π-extension. Noteworthily, the ability to form selectively nanostructures from solution casting and trigger their reorganization on surfaces make these molecules ideal to further program functional materials featuring optimized performances as organic semiconductors, just like their PDI and NDI analogues.

EXPERIMENTAL SECTION

General Experimental Methods. NMR spectra (^{1}H-, ^{13}C-NMR) were recorded on a *Bruker* AVANCE III 600 MHz equipped with an Inverse QCI CryoProbe™ or *Bruker* AVANCE III HD 400 MHz NMR spectrometer equipped with a Broadband multinuclear (BBFO) SmartProbe™ or on a *Bruker* ADVANCE III HD 300 MHz NMR. Chemical shifts are reported in ppm using the solvent residual signal as an internal reference ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm; CD_2Cl_2: δ_H = 5.32 ppm, δ_C = 54.00 ppm; $(CD_3)_2CO$: δ_H = 2.05 ppm, δ_C = 29.84 ppm, 206.26 ppm; $(CD_3)_2SO$: δ_H = 2.50 ppm, δ_C = 39.52 ppm). The resonance multiplicity is described as s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), quint (quintuplet), m (multiplet), and br (broad signal). Coupling constants, *J*, are reported in Hertz. All spectra were recorded at 25 °C unless specified otherwise. In the case of molecules **9**, **10**, **13**^{Oct} the *J* values of defined the dd patterns are close enough that apparent triplets t, thus the two can be mistaken. In such cases we report the resonance multiplicity as dd indicating only one *J* value. **Infrared spectra** (IR) were recorded on a Shimadzu IR Affinity 1S FTIR spectrometer in ATR mode with a diamond mono-crystal. **Mass spectrometry:** (i) High-resolution ESI mass spectra (HRMS) were performed on a Waters LCT HR TOF mass spectrometer in the positive or negative ion mode. (ii) High-resolution MALDI mass spectra (HRMS) were performed on a Waters Synapt G2-Si QTOF mass spectrometer. (iii) High resolution Atmospheric pressure chemical ionization (APCI) and Atmospheric Solids Analysis Probe (ASAP) mass spectrometry was performed on a Waters LCT Premier quadrupole time of flight mass spectrometer operating in the atmospheric pressure chemical ionization mode; all these analyses were carried out at Cardiff University. **Melting points** (m.p.) were measured on a *Gallenkamp* apparatus in open capillary and have not been corrected. **UV-Vis absorption** spectra were recorded on air equilibrated solutions at r.t. with an *Agilent* Cary 5000 UV-Vis-NIR spectrophotometer, using quartz cells with path length of 1.0 cm. **Emission spectra** were recorded on an *Agilent* Cary Eclipse fluorescence spectrofluorometer or with a PerkinElmer LS-50 spectrofluorometer, equipped with a Hamamatsu R928 photomultiplier tube. Quantum yield values in solution of compound **2**^{Per} is calculated using Coumarin 153 in air equilibrated ethanol as a standard (Φ = 0.53)[16] and **1**$^{Oct\text{-}Mes}$, **2**^{Mes} and **2**^{Teg} are calculated using Rhodamine 6G[16] in air equilibrated ethanol as a standard (Φ = 0.94) following the method of Demas and Crosby.[20] **Cyclic Voltammetry** was realized using a Metrohm-Autolab PGSTAT204 potentiostat. **Adsorption silica chromatography columns** (SCC): *Merck* silica gel 60 (40-63 μm) was used. **Chemicals** were purchased from *Sigma Aldrich*, *TCI*, *Acros*, *Fluorochem* and *Alfa Aesar* and used as received, unless otherwise stated. **Solvents** were purchased from *VWR*, *Sigma Aldrich* and *Acros*, and deuterated solvents from *Sigma Aldrich*, *Fluorochem* and *Cambridge Isotope Laboratories* and used as received. THF and CH_2Cl_2 were dried on a *Braun* MB SPS-800 solvent purification system and further dried over activated 4 Å molecular sieves. Anhydrous conditions, when necessary, were achieved by keeping all glassware in oven at 140 °C overnight and then allowed to cool down under vacuum followed by drying the two-neck flask by flaming with heat-gun under vacuum and purging with N_2. The inert atmosphere was maintained using Nitrogen-filled balloons equipped with a syringe and needle that was used to penetrate the silicon stoppers used to close the flask's necks.

Compounds **5**,[10] **14**^{Oct},[10] **25**[7] and **28**[21] were prepared following previously reported synthetic protocol.

5-hydroxy-2-octyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 4^{Oct}**.** In a single-neck round bottom flask, DIPEA (1.81 g, 14.0 mmol) was added to a suspension of commercially available 3-hydroxy-1,8-naphthalic anhydride (1.50 g, 7.00 mmol) in 1,4-dioxane (75 mL). The solution turned red and *n*-octylamine (1.36 g, 10.5 mmol) was added. The reaction mixture was stirred under reflux for 16 hours and a change in colour (brown) was observed. Thus, the solvent was removed under reduced pressure and the solid residue suspended in $HCl_{(aq)}$ (10 % w/w) and extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude material was purified by silica gel chromatography (eluents: pentane:AcOEt 2:1) affording *title compound* **4**^{Oct} (1.71 g, 75 %) as a yellow solid. M.p.: 153 – 154 °C. FTIR (ATR) ν (cm^{-1}): 3371, 2949, 2918, 2850, 1695, 1618, 1516, 1440, 1352, 1284, 1134, 1091, 1062, 1043. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.45 (d, 1H, J = 2.5 Hz), 8.42 (dd, 1H, J

= 7.3, 1.1 Hz), 8.04 (dd, 1H, *J* = 8.3, 1.1 Hz), 7.67 (dd, 1H, *J* = 8.3, 7.3 Hz), 7.60 (d, 1H, *J* = 2.5 Hz), 6.87 (s, 1H), 4.25 – 4.11 (m, 2H), 1.82 – 1.68 (m, 2H), 1.51 – 1.16 (m, 10H), 0.86 (t, 3H, *J* = 6.9 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.8, 164.4, 155.5, 133.5, 132.8, 129.0, 127.5, 123.6, 123.4, 122.6, 122.3, 116.8, 41.0, 31.9, 29.5, 29.4, 28.3, 27.3, 22.8, 14.2. HRMS (ESI-TOF): m/z $[M + H]^+$ Calcd for $C_{20}H_{24}NO_3$ 326.1756; Found 326.1740.

Dimethyl 4-bromo-3-methoxynaphthalene-1,8-dicarboxylate 6. In a single-neck round bottom flask, DBU (7.79 g, 51.2 mmol) was added to a suspension of bromo-derivative **5** (5.00 g, 17.1 mmol) in MeOH (100 mL) at 0 °C. The solution turned yellow and CH_3I (7.24 g, 51.2 mmol) was added. The reaction mixture was allowed to warm up at r.t. and heated under reflux for 16 hours. The volatiles were removed *in vacuo* and the residue taken in CH_2Cl_2. The solution was washed with $HCl_{(aq)}$ (10 % w/w) and $Na_2S_2O_{3(aq)}$, dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude material was purified by crystallization from MeOH, affording *title compound* **6** (4.88 g, 81 %) as a white solid. M.p.: 126 – 129 °C. FTIR (ATR) ν (cm^{-1}): 3024, 2993, 2947, 2846, 1720, 1560, 1435, 1354, 1269, 1074. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.49 (dd, 1H, *J* = 8.7, 1.2 Hz), 7.93 (dd, 1H, *J* = 7.1, 1.2 Hz), 7.77 (s, 1H), 7.60 (dd, 1H, *J* = 8.7, 7.1 Hz), 4.08 (s, 3H), 3.92 (s, 3H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.0, 168.6, 153.2, 134.2, 130.8, 130.6, 130.0, 128.8, 127.1, 123.9, 117.1, 113.2, 57.2, 52.5, 52.4. HRMS (EI-TOF): m/z $[M]^+$ Calcd for $C_{15}H_{13}O_5Br$ 351.9946; found 351.9945.

Dimethyl 4-pinacoloborate-3-methoxynaphthalenic-1,8-dicarboxylate 7. In a single-neck round bottom flask, bromo-derivative **6** (2.0 g, 5.66 mmol) and KOAc (1.66 g, 17.0 mmol) were suspended in 1,4-dioxane (200 mL) and the resulting mixture degassed for 20 minutes by bubbling N_2 under sonication. Subsequently, B_2Pin_2 (1.58 g, 6.22 mmol) and $[Pd(PPh_3)_2Cl_2]$ (198 mg, 0.28 mmol) were added to the reaction mixture. The resulting suspension was degassed for other 20 minutes and heated under reflux for 16 hours under N_2. After cooling down to r.t., the mixture was filtered over celite® and the solvent evaporated under reduced pressure. The crude material was suspended in CH_2Cl_2 and precipitated from petroleum ether, to give *title compound* **7** (1.79 g, 79 %) as a white solid. M.p.: 170 – 178 °C. FTIR (ATR) ν (cm^{-1}): 2978, 2954, 1726, 1342, 1309, 1267, 1138, 1070. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.01 (d, 1H, *J* = 8.2 Hz), 7.85 (d, 1H, *J* = 6.9 Hz), 7.71 (s, 1H), 7.47 (dd, 1H, *J* = 7.8 Hz), 3.96 (s, 3H), 3.90 (s, 3H), 3.89 (s, 3H), 1.47 (s, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 169.6, 169.2, 160.3, 138.4, 132.9, 131.5, 129.9, 128.0, 125.9, 123.0, 116.5, 84.6, 56.8, 52.3, 52.2, 25.0; one peak is missing. HRMS (EI-TOF): m/z $[M]^+$ Calcd for $C_{21}H_{25}O_7B$ 399.1730; Found 399.1734

Tetramethyl 2,2'-dimethoxy-[1,1'-binaphthalene]-4,4',5,5'-tetracarboxylate 8. Method 1. In a single-neck round bottom flask, bromo-derivative **6** (0.50 g, 1.41 mmol) and K_3PO_4 (3.08 g, 14.2 mmol) were suspended in dry 1,4-dioxane (20 mL) and the resulting mixture degassed for 20 minutes by bubbling N_2 under sonication. Subsequently, B_2Pin_2 (197 mg, 0.77 mmol), $[Pd(dba)_2]$ (9.7 mg, 0.02 mmol) and SPhos (13 mg, 0.03 mmol) were added to the reaction mixture. The resulting suspension was degassed for an additional 20 minutes and heated under reflux for 20 hours under N_2. After cooling down to r.t., the mixture was filtered over celite® and the solvent evaporated under reduced pressure. The crude material was purified by silica gel chromatography (eluents: petroleum ether:EtOAc 1:1) affording *title compound* **8** as a white solid (92 mg, 22%).

Method 2. In a single-neck round bottom flask, methoxy-bromo-derivative **6** (1.0 g, 2.83 mmol) and K_3PO_4 (1.84 g, 8.49 mmol) were suspended in a mixture of 1,4-dioxane/H_2O (5/1 v/v, 120 mL) and the resulting mixture degassed for 20 minutes by bubbling N_2 under sonication. Subsequently, boron-derivative **7** (2.26 g, 5.66 mmol), $[Pd(dba)_2]$ (81 mg, 0.14 mmol) and SPhos (116 mg, 0.28 mmol) were added to the reaction mixture. The resulting suspension was degassed for an additional 20 minutes and stirred under reflux for 20 hours under N_2. After cooling down to r.t., the mixture was filtered over celite® and the solvent evaporated under reduced pressure. The crude material was purified by silica gel chromatography (eluents: petroleum ether:EtOAc 1:1) affording *title compound* **8** as a white solid (1.25 g, 81%). M.p.: 229 – 235 °C. FTIR (ATR) ν (cm^{-1}): 2980, 2889, 1716, 1508, 1436, 1340, 1261, 1166, 1145, 1066, 1006. ^{1}H NMR ($(CD_3)_2CO$, 400 MHz): δ 7.92 (s, 2H), 7.75 (dd, 2H, *J* = 7.0, 1.3 Hz), 7.29 (dd, 2H, *J* = 8.6, 7.0 Hz), 7.18 (dd, 2H, *J* = 8.6, 1.3 Hz), 3.84 (s, 6H), 3.81 (s, 6H), 3.75 (s, 6H). ^{13}C NMR ($(CD_3)_2CO$, 101 MHz): δ 169.7, 169.3, 155.2, 135.8, 133.0, 131.5, 129.8, 128.7, 127.0, 123.9, 123.2, 118.2, 57.0, 52.6, 52.4. HRMS (APCI-TOF): m/z $[M]^+$ Calcd for $C_{30}H_{26}O_{10}$ 546.1526; Found 546.1522.

5,5'-dimethoxy-1*H*,1'*H*,3*H*,3'*H*-[6,6'-bibenzo[*de*]isochromene]-1,1',3,3'-tetraone 9. In a single-neck round bottom flask, binaphthyl-tetramethyl ester **8** (1.00 g, 1.83 mmol) and KOH (513 mg, 9.14 mmol) were dissolved in *i*PrOH (50 mL) and stirred under reflux for 13 hours. The solvent was removed under reduced pressure and the solid residue suspended in a mixture of $AcOH/HCl_{(conc)}$ (1:1 v/v, 100 mL) and heated under reflux for an additional 24 hours. The reaction mixture was poured on crushed ice and a dark precipitate was formed. The solid was filtered and dried *in vacuo* to give *title compound* **9** as a brown solid (674 mg, 81%). M.p.: > 300 °C. FTIR (ATR) ν (cm^{-1}): 2980, 2889, 1770, 1730, 1591, 1570, 1510. 1460, 1388, 1344, 1344, 1263, 1149, 1014. ^{1}H NMR ($(CD_3)_2SO$, 300 MHz): δ 8.51 (s, 2H), 8.41 (d, 2H, *J* = 7.1 Hz), 7.69 (dd, 2H, *J* = 7.9 Hz), 7.45 (d, 2H, *J* = 8.5 Hz), 3.91 (s, 6H). ^{13}C NMR ($(CD_3)_2SO$, 75 MHz): δ 160.6, 160.5, 155.5, 131.7, 131.3, 130.4, 128.7, 125.5, 124.5, 121.3, 119.7, 118.4, 56.9. HRMS (APCI-TOF): m/z $[M + H]^+$ Calcd for $C_{26}H_{15}O_8$ 455.0767; Found 455.0765.

5,5'-dihydroxy-1*H*,1'*H*,3*H*,3'*H*-[6,6'-bibenzo[*de*]isochromene]-1,1',3,3'-tetraone 10. In a single-neck round bottom flask, binaphthyl-dianhydride **9** (200 mg, 0.44 mmol) was suspended in AcOH/HBr (48% w/w aq.) (1:1 v/v, 20 mL) and heated at 126 °C for 24 hours. After cooling down to r.t., the volatiles were removed. The solid residue was suspended in H_2O and filtered to give *title compound* **10** as a dark solid (185 mg, quantitative). M.p.: >300 °C. FTIR (ATR) ν (cm^{-1}): 3055, 2980, 2889, 2260,

1768, 1728, 1585, 1508, 1402, 1257, 1178, 1145,1085, 1018. ^{1}H NMR ($(CD_3)_2SO$, 300 MHz): δ 10.77 (s, 2H), 8.33 (d, 4H, J = 6.2 Hz), 7.66 (dd, 2H, J = 7.8 Hz), 7.47 (d, 2H, J = 8.5 Hz). ^{13}C NMR ($(CD_3)_2SO$, 75 MHz): δ 160.7, 160.5, 154.2, 132.3, 131.4, 129.3, 128.1, 124.8, 123.1, 122.4, 120.4, 119.3. HRMS (EI-TOF): m/z $[M]^+$ Calcd for $C_{24}H_{10}O_8$ 426.0376; Found 426.0381.

5,5'-dimethoxy-2,2'-dioctyl-1*H*,1'*H*-[6,6'-bibenzo[*de*]isoquinoline]-1,1',3,3'(2*H*,2'*H*)-tetraone 13^{Oct}. To a stirred solution of 2,2'-dihydroxy-[1,1'-binaphthalene]-dianhydride **10** (200 mg, 0.47 mmol) in 1,4-dioxane (10 mL), *n*-octylamine (133 mg, 1.03 mmol) and DIPEA (0.13 mg, 179 µL, 1.03 mmol) were added and the reaction mixture stirred at *ca.* 101 °C for 24 hours under inert atmosphere. The volatiles were removed *in vacuo*, the remaining material dissolved in EtOAc (10 mL) and the resulting solution passed through a thin pad of silica (EtOAc) to give *title compound* **13**^{Oct} as a yellow powder (280 mg, 92%). M.p.: 256 – 258 °C. ^{1}H NMR ($(CD_3)_2SO$, 300 MHz): δ 10.46 (s, 2H), 8.33 (s, 2H), 8.28 (dd, 2H, J = 7.1 Hz), 7.58 (dd, 2H, J = 7.9 Hz), 7.42 (dd, 2H, J = 8.4 Hz), 4.10 – 4.06 (m, 4H), 1.69 – 1.64 (m, 4H), 1.33 – 1.26 (m, 20H), 0.86 (t, 6H, J = 6.6 Hz). HRMS (MALDI-TOF): m/z $[M + H]^+$ Calcd for $C_{40}H_{45}N_2O_6$ 649.3278; Found 649.3251. Characterization in accordance with data reported in the literature.[10]

***N,N'*-bis(octyl)-3,4,8,10-*peri*-xanthenoxanthenetetracarboxylic-diimide 1^{Oct}. Imidation-Pummer (IP) strategy. Method 1.** Compound **4**^{Oct} (130 mg, 0.40 mmol) and CuCl (12.0 mg, 0.12 mmol) were dissolved in DMSO (20 mL). The reaction mixture was heated at 120 °C under air for 24 hours and thus diluted with H_2O (10 mL). The precipitated solid material was collected by filtration, washed with H_2O (10 mL), MeOH (2 mL) and then dissolved in CH_2Cl_2 (20 mL). The dissolved product was chromatographed on silica (eluents: CH_2Cl_2:EtOH 20:1) to give *title compound* **1**^{Oct} as a red powder (55.0 mg, 43%).

Method 2. Compound **4**^{Oct} (74.6 mg, 0.23 mmol), pivalic acid (47.0 mg, 0.46 mmol) and CuI (132 mg, 0.69 mmol) were dissolved in DMSO (9 mL). The reaction mixture was heated at 150 °C under air for 5 hours. The reaction mixture was cooled down to r.t., diluted with H_2O (20 mL) and extracted with $CHCl_3$ (2 × 100 mL). The combined organic layers were dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude material was precipitated in MeOH, filtered and washed with MeOH. The residual solid was chromatographed on silica (eluents: CH_2Cl_2:MeOH 100:0 to 99:1) to give *title compound* **1**^{Oct} as a red powder (14.6 mg, 20%).

SIP strategy: C-O cyclisation.

Method 1. Compound **13**^{Oct} (200 mg, 0.31 mmol) and CuCl (9.00 mg, 0.09 mmol) were dissolved in DMSO (10 mL). The reaction mixture was heated at 120 °C under air for 24 hours and then diluted with water (10 mL). The precipitated solid material was collected by filtration, washed with H_2O (10 mL), MeOH (2 mL) and then dissolved in CH_2Cl_2 (20 mL). The dissolved product was chromatographed on silica (eluents: CH_2Cl_2:EtOH 20:1) to give *title compound* **1**^{Oct} as a red powder (81.0 mg, 41%).

Method 2. Compound **13**^{Oct} (150 mg, 0.23 mmol), pivalic acid (47.0 mg, 0.46 mmol) and CuI (132 mg, 0.69 mmol) were dissolved in DMSO (9 mL). The reaction mixture was heated at 120 °C under air for 5 hours. The reaction mixture was cooled down to r.t., diluted with water (40 mL) and extracted with $CHCl_3$ (2 ×100 mL). The combined organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude material was chromatographed on silica (CH_2Cl_2:EtOH 20:1) to give *title compound* **1**^{Oct} as a red powder (115 mg, 77%). M.p.: > 300 °C. FTIR (ATR) ν (cm^{-1}): 1696, 1658, 1630, 1596, 1379, 1364, 1342, 1269, 1243, 1122, 1087. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.38 (d, 2H, J = 8.3), 8.23 (s, 2H), 7.16 (d, 2H, J = 8.3), 4.17 – 4.12 (m, 4H), 1.74 – 1.69 (m, 4H), 1.38 – 1.25 (m, 20H), 0.89 (t, 6H, J = 6.9). ^{13}C NMR ($CDCl_3$, 150 MHz): δ 163.0, 162.7, 156.7, 145.8, 134.3, 126.6, 123.9, 121.4, 119.1, 116.59, 116.56, 111.8, 41.0, 32.0, 29.5, 29.4, 28.2, 27.3, 22.8, 14.3. HRMS (MALDI-TOF): m/z $[M]^+$ Calcd for $C_{40}H_{40}N_2O_6$ 644.2886; Found 644.2866. Characterization in accordance with data reported in the literature.[10]

Dimethyl 3-methoxy-4-(5-methoxy-2-octyl-1,3-dioxo-2,3-dihydro-1*H*-benzo[*de*]isoquinolin-6-yl)naphthalene-1,8-dicarboxylate 15^{Oct}. Compound 14^{Oct} (0.50 g, 1.20 mmol) and K_3PO_4 (0.76 g, 3.59 mmol) were suspended in a mixture of 1,4-dioxane/H_2O (5/1 v/v, 60 mL) and the resulting mixture degassed for 20 minutes by bubbling N_2 under sonication. Subsequently, dimethyl 4-pinacoloborate-3-methoxynaphthalenic-1,8-dicarboxylate 7 (0.96 g, 2.39 mmol), $[Pd(dba)_2]$ (34.0 mg, 0.06 mmol) and SPhos (49.0 mg, 0.12 mmol) were added to the reaction mixture. The resulting suspension was stirred under reflux for 24 hours under inert atmosphere. The reaction mixture was cooled down to r.t. and the volatiles removed *in vacuo*. The crude material was dissolved in CH_2Cl_2 (20 mL) and chromatographed on SiO_2 (eluents: CH_2Cl_2 to CH_2Cl_2:MeOH 10:1) to give crude product which was recrystallised from MeOH affording *title compound* 15^{Oct} as beige prisms (431mg, 59%). M.p.: 122 – 128 °C (from MeOH). FTIR (ATR) ν (cm^{-1}): 2951, 2926, 2849, 1728, 1697, 1655, 1614, 1589, 1508, 1460, 1437, 1396, 1342, 1265, 1229, 1217, 1196, 1173, 1138, 1128, 1086, 1069, 1053, 1024, 978, 962, 928, 891, 876, 841, 824, 781, 766, 746, 737, 714, 696, 671, 608, 584, 554, 490, 447, 430, 403. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.51 (s, 1H), 8.44 (dd, 1H, J = 7.1, 1.3 Hz), 7.95 (s, 1H), 7.86 (dd, 1H, J = 6.9, 1.4 Hz), 7.48 (dd, 1H, J = 8.5, 7.1 Hz), 7.39 (dd, 1H, J = 8.5, 1.3 Hz), 7.30 – 7.15 (m, 2H), 4.26 – 4.19 (m, 2H), 3.99 (s, 3H), 3.97 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H), 1.77 (quint, 2H, J = 7.6 Hz), 1.51-1.24 (m, 10H), 0.88 (t, 3H, J = 6.8 Hz). ^{13}C NMR (APT, $CDCl_3$, 75 MHz): δ 169.4 (s), 169.0 (s), 164.2 (s), 164.1 (s), 155.9 (s), 154.0 (s), 134.8 (s), 132.6 (s), 131.9 (s), 131.1 (d), 130.0 (s), 129.2 (d), 129.1 (d), 128.2 (d), 127.6 (d), 126.2 (d), 125.6 (s), 124.2 (s), 123.9 (s), 123.1 (s), 122.9 (s), 121.7 (s), 117.4 (d), 117.1 (d), 56.73 (CH_3), 56.68(CH_3), 52.4 (CH_3), 52.3 (CH_3), 40.6 (CH_2), 31.9 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.2 (CH_2), 27.2 (CH_2), 22.7 (CH_2), 14.1 (CH_3). HRMS (ASAP-TOF): m/z $[M + H]^+$ Calcd for $C_{36}H_{38}NO_8$ 612.2597; Found 612.2597.

5-methoxy-6-(5-methoxy-1,3-dioxo-1*H*,3*H*-benzo[*de*]isochromen-6-yl)-2-octyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 16^{Oct}. A solution of compound **15^{Oct}** (250 mg, 0.41 mmol) in TFA (6 mL) was stirred at *ca.* 73 °C for 12 hours. After cooling down to r.t, the volatiles were removed *in vacuo*, the solid residue was dissolved in CH_2Cl_2 (20 mL) and chromatographed on silica (eluents: hexane:EtOAc 1:1) to give *title compound* **16^{Oct}** as pale yellow powder (202 mg, 87%). M.p.: 210 – 215 °C (from EtOH). FTIR (ATR) *ν* (cm^{-1}): 3123, 3080, 2955, 2926, 2853, 1778, 1736, 1697, 1659, 1616, 1591, 1576, 1514, 1464, 1441, 1400, 1346, 1331, 1292, 1263, 1238, 1215, 1190, 1180, 1142, 1107, 1086, 1051, 1030, 1011, 970, 949, 895, 883, 854, 831, 779, 743, 708, 696, 675, 660, 590, 577, 554, 528, 484, 444, 436, 430, 420. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 8.54 (s, 1H), 8.53 (s, 1H), 8.52 – 8.45 (m, 2H), 7.60 – 7.45 (m, 3H), 7.34 (dd, 1H, *J* = 8.5, 1.1 Hz), 4.26 – 4.20 (m, 2H), 3.91 (s, 3H), 3.90 (s, 3H), 1.77 (quint, 2H, *J* = 7.6 Hz), 1.50 – 1.23 (m, 10H), 0.89 (t, 3H, *J* = 6.7 Hz). ^{13}C NMR (APT, $CDCl_3$, 75 MHz): *δ* 164.2 (s), 164.0 (s), 160.7 (s), 160.5 (s), 156.1 (s), 155.7 (s), 132.7 (s), 132.5 (d), 132.2 (s), 131.6 (d), 130.6 (d), 129.4 (d), 128.3 (d), 128.1 (d), 126.8 (s), 126.1 (s), 125.0 (s), 124.0 (s), 123.6 (s), 123.2 (s), 120.5 (s), 119.1 (s), 118.9 (d), 117.0 (d), 57.0 (*C*H_3), 56.9 (*C*H_3), 40.8 (*C*H_2), 32.0 (*C*H_2), 29.5 (*C*H_2), 29.4 (*C*H_2), 28.3 (*C*H_2), 27.3 (*C*H_2), 22.8 (*C*H_2), 14.2 (*C*H_3). HRMS (APCI-TOF): m/z [M + H]$^+$ Calcd for $C_{34}H_{32}NO_7$ 566.2179; Found 566.2186.

5-hydroxy-6-(5-hydroxy-1,3-dioxo-1*H*,3*H*-benzo[*de*]isochromen-6-yl)-2-octyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 17^{Oct}. To the stirred solution of compound **16^{Oct}** (224 mg, 0.40 mmol) in CH_2Cl_2 (5 mL) BBr_3 (1M solution in CH_2Cl_2, 2 mL, 2.0 mmol) was added at *ca.* 0 °C. The reaction mixture was allowed to warm up to r.t and stirred for 12 hours. The reaction mixture was cooled down to *ca.* 0 °C and quenched with crushed ice. The solidified reaction mixture was dispersed in petroleum ether (10 mL) and the solid material collected by filtration. The crude solid product was dissolved in EtOAc (20 mL), passed through a thin pad of silica (EtOAc) and the volatiles were removed *in vacuo* to give *title compound* **17^{Oct}** as yellow powder (212 mg, 99%). M.p.: 278 – 293 °C (from EtOH). FTIR (ATR) *ν* (cm^{-1}): 3246, 2949, 2924, 2855, 1769 1736, 1701, 1680, 1639, 1611, 1593, 1582, 1535, 1512, 1466, 1452, 1408, 1385, 1368, 1341, 1321, 1287, 1265, 1221, 1188, 1167, 1134, 1099, 1082, 1063, 1043, 1001, 934, 912, 901, 883, 866, 856, 831, 783, 754, 743, 718, 704, 692, 664, 638, 598, 584, 563, 554, 540, 530, 500, 482, 465, 449, 444, 432, 420, 403. ^{1}H NMR ($(CD_3)_2SO$, 300 MHz): *δ* 10.61 (brs, 2H), 8.39-8.23 (m, 4H), 7.69-7.55 (m, 2H), 7.51 (d, 1H, *J* = 8.4 Hz), 7.38 (d, 1H, *J* = 8.4 Hz), 4.14 – 4.00 (m, 2H), 1.73 – 1.58 (m, 2H), 1.42-1.17 (m, 10H), 0.86 (t, 3H, *J* = 6.3 Hz). ^{13}CNMR (APT, $(CD_3)_2CO$, 75 MHz): 1 *C*H_2 missing, *δ* 164.5 (s), 164.2 (s), 161.5 (s), 161.3 (s), 155.3 (s), 155.1 (s), 134.1 (s), 133.8 (s), 132.9 (d), 131.2 (d), 130.7 (d), 129.0 (d), 128.7 (d), 128.7 (d), 126.5 (s), 125.6 (s), 124.5 (d), 124.3 (s), 124.0 (s), 123.9 (s), 122.7 (d), 121.7 (s), 121.3 (s), 120.3 (s), 40.9 (*C*H_2), 32.6 (*C*H_2), 30.0 (*C*H_2), 28.8 (*C*H_2), 27.9 (*C*H_2), 23.3 (*C*H_2), 14.4 (*C*H_3). HRMS (APCI-TOF): m/z [M + H]$^+$ Calcd for $C_{32}H_{27}NO_7$ 538.1866; Found 538.1867.

5,5'-dihydroxy-2-mesityl-2'-octyl-1*H*,1'*H*-[6,6'-bibenzo[*de*]isoquinoline]-1,1',3,3'(2*H*,2'*H*)-tetraone 13$^{Oct\text{-}Mes}$. 2,4,6-Trimethylaniline (50.0 mg, 0.37 mmol), compound **17^{Oct}** (100 mg, 0.19 mmol) and imidazole (1.00 g) were stirred at *ca.* 150 °C for 12 hours under inert atmosphere. After cooling down to r.t., the reaction mixture was suspended in $HCl_{(aq)}$ (10 % w/w, 10 mL). The solid material was collected by filtration, washed with $HCl_{(aq)}$ (10 % w/w, 10 mL), H_2O (10 mL) and dried. The crude material was chromatographed on silica (eluent: CH_2Cl_2) to give *title compound* **13$^{Oct\text{-}Mes}$** as orange powder (89.0 mg, 73%). M.p.: 215 – 218 °C. FTIR (ATR) *ν* (cm^{-1}): 3310, 2953, 2924, 2855, 1699 1649, 1612, 1587, 1512, 1483, 1458, 1437, 1404, 1369, 1339, 1306, 1271, 1233, 1211, 1173, 1152, 1096, 1063, 1032, 1011, 988, 955, 907, 887, 849, 824, 783, 758, 745, 718, 706, 694, 671, 662, 646, 629, 590, 571, 559, 530, 509, 484, 473, 447, 413, 405. ^{1}H NMR ($CDCl_3$, 300 MHz): two O*H* signals are missing; *δ* 8.54 (s, 1H), 8.50 (dd, 1H, *J* = 7.1, 1.1 Hz), 8.41 (s, 1H), 8.38 – 8.31 (m, 1H), 7.61 – 7.42 (m, 4H), 6.96 (d, 2H, *J* = 2.6 Hz), 3.97 – 3.83 (m, 2H), 2.25 (s, 3H), 2.12 (s, 3H), 2.04 (s, 3H), 1.57 (quint, 2H, *J* = 7.0 Hz), 1.35 – 1.14 (m, 10H), 0.83 (t, 3H, *J* = 6.8 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): 1 C_q and 1 C_{tert} missing, δ 164.0 (s), 163.8 (s), 163.7 (s), 163.6 (s), 153.9 (s), 153.8 (s), 138.8 (s), 135.2 (s), 132.7 (s), 132.7 (s), 131.1 (d), 131.0 (s), 130.9 (d), 129.6 (d), 129.3 (d), 128.4 (d), 128.3 (d), 125.0 (s), 124.6 (s), 123.8 (s), 123.5 (d), 123.1 (s), 123.0 (d), 122.7 (s), 120.1 (s), 119.9 (s), 40.7 (*C*H_2), 31.9 (*C*H_2), 29.4 (*C*H_2), 29.3 (*C*H_2), 28.1 (*C*H_2), 27.2 (*C*H_2), 22.8 (*C*H_2), 21.3 (*C*H_3), 18.0 (*C*H_3), 17.9 (*C*H_3), 14.2 (*C*H_3). HRMS (APCI-TOF): m/z [M + H]$^+$ Calcd for $C_{41}H_{39}N_2O_6$ 655.2808; Found 655.2807.

***N*-mesityl, *N'*-octyl-3,4,8,10-*peri*-xanthenoxanthenetetracarboxylic-diimide 1$^{Oct\text{-}Mes}$.** Compound **13$^{Oct\text{-}Mes}$** (70.0 mg, 0.11 mmol), pivalic acid (22.0 mg, 0.21 mmol) and CuI (60.0 mg, 0.32 mmol) were dissolved in DMSO (10 mL). The reaction mixture was heated at 120 °C under air for 12 hours and then diluted with H_2O (10 mL). The precipitated solid material was collected by filtration, washed with H_2O (10 mL), MeOH (2 mL) and then dissolved in CH_2Cl_2 (5 mL). The dissolved product was chromatographed on silica (eluents: CH_2Cl_2:EtOH 10:0.5) to give *title compound* **1$^{Oct\text{-}Mes}$** as red powder (62.0 mg, 89%). M.p.: 265 - 293 °C. FTIR (ATR) *ν* (cm^{-1}): 3080, 3051, 2953, 2924 2855, 1707, 1694, 1659, 1630, 1597, 1582, 1560, 1506, 1485, 1466, 1458, 1410, 1360, 1346, 1314, 1298, 1267, 1242, 1204, 1194, 1179, 1171, 1119, 1088, 1053, 1036, 1015, 959, 945, 907, 870, 853, 839, 808, 758, 741, 731, 718, 694, 677, 656, 623, 613, 600, 571, 561, 534, 523, 509, 488, 434. ^{1}H NMR ($CDCl_3$, 300 MHz): *δ* 8.44 (d, 1H, *J* = 8.3 Hz), 8.34 (d, 1H, *J* = 8.3 Hz), 8.27 (s, 1H), 8.19 (s, 1H), 7.18 (d, 1H, *J* = 8.3 Hz), 7.13 (d, 1H, *J* = 8.3 Hz), 7.04 (s, 2H), 4.16 – 4.07 (m, 2H), 2.36 (s, 3H), 2.10 (s, 6H), 1.68 (quint, 2H, *J* = 7.3 Hz), 1.43 – 1.22 (m, 10H), 0.88 (t, 3H, *J* = 6.7 Hz). ^{13}C NMR (APT, $CDCl_3$, 75 MHz): δ 162.9 (s), 162.6 (s), 162.5 (s), 162.1 (s), 157.0 (s), 156.6 (s), 145.8 (s), 145.8 (s), 138.8 (s), 135.1 (s), 134.7 (d), 134.3 (d), 131.3 (s), 129.6 (d), 127.5 (s), 126.6 (s), 124.0 (s), 124.0 (s), 121.8 (d), 121.3 (d), 119.3 (s), 119.0 (s), 116.8 (s), 116.7 (s), 116.6 (s), 116.4 (s), 111.9 (d), 111.8 (d), 41.0 (*C*H_2), 32.0 (*C*H_2), 29.5 (*C*H_2), 29.4 (*C*H_2), 28.2 (*C*H_2), 27.3 (*C*H_2), 22.8 (*C*H_2), 21.3 (*C*H_3), 17.9 (*C*H_3), 14.2 (*C*H_3). HRMS (APCI-TOF): m/z [M + H]$^+$ Calcd for $C_{41}H_{35}N_2O_6$ 651.2495; Found 651.2491.

Dimethyl 2,2'-dimethoxy-[1,1'-binaphthalene]-4,5-dicarboxylate 18. **Method 1.** In a single-neck round bottom flask, methoxy-bromo-derivative **6** (1.66 g, 4.72 mmol) and K_3PO_4 (3.08 g, 14.2 mmol) were suspended in 1,4-dioxane (55 mL) and the resulting mixture degassed for 20 minutes by bubbling N_2 under sonication. Subsequently, 2-methoxy-naphthaleneboronic acid (1.91 g, 9.43 mmol), [Pd(dba)$_2$] (135 mg, 0.23 mmol) and SPhos (193 mg, 0.47 mmol) were added to the reaction mixture. The resulting suspension was degassed for additional 20 minutes and heated under reflux for 24 hours under N_2. After cooling down to r.t., the reaction mixture was filtered over celite® and the solvent evaporated under reduced pressure. The crude material was purified by silica gel chromatography (eluents: petroleum ether:EtOAc, 3:1) to give *title compound* **18** as a white solid (2.01 g, quantitative).

Method 2. In a single-neck round bottom flask, 1-bromo-2-methoxynaphthalene **28** (100 mg, 0.42 mmol) and K_3PO_4 (276 mg, 1.27 mmol) were suspended in 1,4-dioxane/H_2O (5/1 v/v, 12 mL) and the resulting mixture degassed for 20 minutes bubbling N_2 under sonication. Subsequently, boron-derivative **7** (339 mg, 0.84 mmol), [Pd(dba)$_2$] (12.0 mg, 0.02 mmol) and SPhos (17.0 mg, 0.04 mmol) were added to the reaction mixture. The resulting suspension was degassed for other 20 minutes and stirred under reflux for 16 hours under N_2. After cooling down to r.t., the reaction mixture was filtered over celite® and the solvent evaporated under reduced pressure. The crude material was purified by silica gel chromatography (eluents: petroleum ether: EtOAc 3:1) to give *title compound* **18** as a white solid (360 mg, quantitative). M.p.: 201 – 205 °C. FTIR (ATR) ν (cm^{-1}): 3066, 2947, 2843, 1708, 1583, 1508, 1431, 1267, 1242, 1139, 1112, 1085, 1058.92. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.04 (d, 1H, J = 9.2 Hz), 7.95 (s, 1H), 7.90 (d, 1H, J = 8.4 Hz), 7.81 (dd, 1H, J = 6.8, 1.6 Hz), 7.48 (d, 1H, J = 9.2 Hz), 7.39 – 7.17 (m, 4H), 7.05 – 6.97 (m, 1H), 3.95 (s, 3H), 3.91 (s, 3H), 3.82 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ 169.9, 169.5, 155.4, 154.8, 135.8, 134.1, 131.5, 130.6, 130.4, 130.1, 129.6, 128.6, 128.4, 127.2, 126.2, 125.2, 124.4, 124.2, 123.5, 118.4, 118.1, 114.2, 57.2, 57.0, 52.7, 52.6. HRMS (EI-TOF): (m/z) [M]$^+$ Calcd for $C_{26}H_{22}O_6$ 430.1416; Found 430.1423.

5-methoxy-6-(2-methoxynaphthalen-1-yl)-1*H*,3*H*-benzo[*de*]isochromene-1,3-dione 19. In a single-neck round bottom flask, binaphthyl-dimethyl ester-derivative **18** (910 mg, 2.11 mmol) and KOH (237 mg, 4.22 mmol) were dissolved in *i*PrOH (20 mL) and stirred under reflux for 13 hours. After cooling down to r.t., the solvent was removed *in vacuo* and the solid residue suspended in a mixture of AcOH:$HCl_{(conc)}$ (4:1 v/v, 25 mL) and stirred under reflux for 24 hours. The solvent was evaporated under reduced pressure. The crude material was purified by silica gel chromatography (eluents: petroleum ether:EtOAc 3:2) to give *title compound* **19** as a yellow solid (696 mg, 86%). M.p.: 234 – 237 °C. FTIR (ATR) ν (cm^{-1}): 3057, 2916, 2916, 2846, 1766, 1728, 1591, 1506, 1406, 1346, 1267, 1141, 1078, 1058, 1001. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 8.51 (s, 1H), 8.45 (dd, 1H, J = 6.8, 1.2 Hz), 8.08 (d, 1H, J = 9.0 Hz), 7.92 (d, 1H, J = 8.2 Hz), 7.61 – 7.47 (m, 3H), 7.39 – 7.33 (m, 1H), 7.29 – 7.22 (m, 1H), 6.98 – 6.94 (m, 1H), 3.92 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (CD_2Cl_2, 101 MHz): δ 161.3, 161.3, 156.8, 155.3, 133.7, 133.6, 133.6, 131.7 131.3, 129.8, 129.5, 128.8, 128.1, 127.6, 126.6, 124.7, 124.4, 119.9, 119.4, 119.3, 116.8, 114.0, 57.4, 56.9. HRMS (EI-TOF): m/z [M]$^+$ Calcd for $C_{24}H_{16}O_5$ 384.0998; Found 384.0992.

5-hydroxy-6-(2-hydroxynaphthalen-1-yl)-1*H*,3*H*-benzo[*de*]isochromene-1,3-dione 20. In an oven dried single-neck round bottom flask, methoxy derivative **19** (1.00 g, 2.60 mmol) was dissolved in dry CH_2Cl_2 (30 mL). The solution was cooled down to 0 °C and BBr_3 (1 M in CH_2Cl_2, 26.0 mL, 26.0 mmol) added. The resulting solution was stirred at r.t. for 30 hours. The reaction mixture was poured on crushed ice and extracted with EtOAc. The organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure to yield *title compound* **20** as a yellow solid (903 mg, quantitative). M.p.: 238 – 242 °C. FTIR (ATR) ν (cm^{-1}): 3402, 2980, 2920, 1776, 1705, 1593, 1510, 1406, 1375, 1269 1217, 1134, 1062. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.46 (dd, 1H, J = 4.9, 3.5 Hz), 8.43 (s, 1H), 8.07 (d, 1H, J = 8.9 Hz), 7.96 (d, 1H, J = 7.9 Hz), 7.62 (s, 1H), 7.61 (d, 1H, J = 1.4 Hz), 7.47 – 7.31 (m, 3H), 7.03 (d, 1H, J = 8.4 Hz), 5.65 (s, 1H), 5.28 (s, 1H). ^{13}C NMR ($(CD_3)_2CO$, 101 MHz): δ 161.4, 161.2, 155.4, 154.1, 134.5, 134.3, 133.1, 131.3, 130.2, 129.5, 128.9, 128.3, 127.4, 126.4, 125.6, 124.5, 124.5, 123.8, 120.6, 119.9, 119.1, 113.1. HRMS (EI-TOF): m/z [M]$^+$ Calcd for $C_{22}H_{12}O_5$ 356.0685; Found 356.0671.

5-hydroxy-6-(2-hydroxynaphthalen-1-yl)-2-octyl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 21^{Oct}. In a single-neck round bottom flask, DIPEA (144 mg, 1.11 mmol) was added to a suspension of dihydroxy-binaphthyl-anhydride **20** (200 mg, 0.56 mmol) and *n*-octylamine (108 mg, 0.84 mmol) in 1,4-dioxane (75 mL). The reaction mixture was stirred under reflux for 20 hours. After cooling down to r.t., the solvent was evaporated under reduced pressure and the solid residue suspended in $HCl_{(aq)}$ (10 % w/w) and extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude was purified by silica gel chromatography (eluents: hexane:EtOAc 5:2) to give *title compound* **21^{Oct}** as a yellow solid (256 mg, 97%). M.p.: 166 – 167 °C. ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.32 (s, 1H), 8.30 (dd, 1H, J = 5.3, 3.2 Hz), 8.05 (d, 1H, J = 8.6 Hz), 7.94 (d, 1H, J = 8.0 Hz), 7.54 – 7.48 (m, 2H), 7.43 – 7.38 (m, 2H), 7.34 – 7.29 (m, 1H), 7.05 – 7.01 (m, 1H), 5.73 (s, 1H), 5.58 (s, 1H), 4.07 – 4.02 (m, 2H), 1.73 – 1.63 (m, 2H), 1.42 – 1.29 (m, 10H), 0.88 (t, 3H, J = 6.8 Hz). ^{13}C NMR (CD_2Cl_2, 75 MHz): δ 164.5, 163.9, 154.1, 153.5, 133.7, 133.2, 132.6, 131.3, 130.0, 129.1, 128.6, 128.2, 125.30, 125.27, 124.8, 124.5, 124.2, 123.4, 122.4, 120.5, 118.9, 110.3, 40.9, 32.4, 29.9, 29.8, 28.5, 27.6, 23.2, 14.4. Characterization in accordance with data reported in the literature.[10]

5-hydroxy-2-(2-(2-(2-hydroxyethoxy)ethoxy)ethyl)-6-(2-hydroxynaphthalen-1-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 21^{Teg}. In a single-neck round-bottomed flask, DIPEA (108 mg, 0.84 mmol) was added to a suspension of dihydroxy-binaphthyl-anhydride **20** (150 mg, 0.42 mmol) and 2-(2-(2-aminoethoxy)ethoxy)ethan-1-ol (94.0 mg, 0.63 mmol) in

1,4-dioxane (10 mL). The reaction mixture was stirred under reflux for 20 hours. After cooling down to r.t., the solvent was evaporated under reduced pressure and the solid residue suspended in $HCl_{(aq)}$ (10 % w/w) and extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude was purified by silica gel chromatography (eluent: EtOAc) to give *title compound* **21^{Oct}** as a yellow solid (170 mg, 83%). M.p.: 148 – 152 °C. FTIR (ATR) ν (cm^{-1}): 3314, 2951, 2920, 2868, 1695, 1651, 1593, 1508, 1406, 1340, 1273, 1229, 1101, 1063, 1024, 816, 781, 746, 689, 579, 540, 498, 424, 417, 405. ^{1}H NMR ($CDCl_3$, 300 MHz): one O*H* peak is missing, δ 8.34 (s, 1H), 8.24 (d, 1H, *J* = 5.9 Hz), 7.95 (d, 1H, *J* = 8.9 Hz), 7.87 (d, 1H, *J* = 7.6 Hz), 7.55 (d, 1H, *J* = 7.6 Hz), 7.46 – 7.26 (m, 4H), 7.03 (d, 1H, *J* = 8.4 Hz), 7.01 (br, 1H), 6.66 (br, 1H), 4.33 – 4.31 (m, 2H), 3.77 (t, 2H, *J* = 5.3 Hz), 3.61 – 3.31 (m, 8H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.4, 164.0, 154.1, 153.1, 133.4, 133.2, 131.6, 131.6, 129.2, 128.9, 128.5, 127.9, 127.5, 124.1, 124.0, 123.8, 122.8, 122.3, 122.0, 118.9, 111.2, 72.2, 70.2, 67.6, 61.7, 39.2, one aliphatic peak and one aromatic peak are missing, probably due to overlap. HRMS (APCI-TOF): (m/z) $[M + H]^+$ Calcd for $C_{28}H_{26}NO_7$ 488.1709; Found 488.1713.

5-hydroxy-6-(2-hydroxynaphthalen-1-yl)-2-mesityl-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 21^{Mes}. In a single-neck round bottom flask, imidazole (344 mg, 5.301 mmol) was added to a mixture of dihydroxy-binaphthyl-anhydride **20** (150 mg, 0.42 mmol) and 2,4,6-trimethylaniline (68.0 mg, 0.50 mmol). The reaction mixture was stirred at 130 °C for 3 hours under N_2. After cooling down to r.t., $HCl_{(aq)}$ (10 % w/w) was added and the resulting solution was extracted with CH_2Cl_2. The combined organic layers were washed with H_2O, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude was purified by silica gel chromatography (eluents: CH_2Cl_2:MeOH 100:0 to 99:1) to give *title compound* **21^{Mes}** as a yellow solid (162 mg, 81%). M.p.: decomposes > 192 °C. FTIR (ATR) ν (cm^{-1}): 3343, 2918, 1699, 1653, 1616, 1589, 1558, 1541, 1508, 1489, 1435, 1404, 1375, 1344, 1273, 1234, 1209, 1005, 976, 939, 906, 887, 851, 814, 783, 727, 708, 646, 527, 476. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.47 (dd, 1H, *J* = 6.7, 1.9 Hz), 8.44 (s, 1H), 7.96 – 7.8688 (m, 2H), 7.59 – 7.51 (m, 2H), 7.42 – 7.30 (m, 2H), 7.54 (d, 1H, *J* = 8.9 Hz), 7.09 (d, 1H, *J* = 8.3 Hz), 7.01 (d, 2H, *J* = 5.2 Hz), 5.85 (br, 2H), 2.30 (s, 3H), 2.16 (s, 3H), 2.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 164.0, 163.5, 153.5, 152.7, 138.7, 135.3, 135.2, 133.3, 132.9, 132.0, 131.8, 131.1, 129.5, 129.4, 128.7, 128.1, 127.9, 124.8, 124.5, 124.4, 124.1, 122.9, 122.9, 121.4, 118.2, 110.3, 21.3, 18.0, 17.9, two peaks are missing probably due to overlap. HRMS (APCI-TOF): (m/z) $[M + H]^+$ Calcd for $C_{31}H_{24}NO_4$ 474.1705; Found 474.1703.

***N*-octyl-3,4-*peri*-xanthenoxanthene-dicarboxylic-imide 2^{Oct}, PXXMI.**[10] In a single-neck round bottom flask, compound **21^{Oct}** (120 mg, 0.25 mmol), pivalic acid (52.0 mg, 0.51 mmol) and CuI (146 mg, 0.77 mmol) were dissolved in DMSO (4 mL). The reaction mixture was heated at 120 °C under air for 5 hours. The resulting mixture was poured into H_2O and extracted with $CHCl_3$. The combined organic layers were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude material was purified by silica gel chromatography (eluent: CH_2Cl_2) affording *title compound* **21^{Oct}** as a red solid (102 mg, 86%). M.p.: 217 – 233 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.08 (d, 1H, *J* = 8.4 Hz), 7.69 (s, 1H), 7.33 (d, 1H, *J* = 9.2 Hz), 7.12 – 7.02 (m, 2H), 6.91 (d, 1H, *J* = 9.2 Hz), 6.78 (d, 1H, *J* = 8.3 Hz), 6.59 (d, 1H, *J* = 7.3 Hz), 4.09 – 4.04 (m, 2H), 1.72 – 1.64 (m, 2H), 1.44 – 1.25 (m, 10H), 0.89 (t, 3H, *J* = 6.8 Hz). ^{13}C NMR (CD_2Cl_2, 151 MHz): δ 163.4, 163.1, 157.2, 152.6, 145.6, 145.5, 133.5, 131.9, 129.7, 128.8, 126.6, 121.7, 121.2, 121.1, 120.6, 119.2, 118.6, 117.7, 116.2, 110.59, 110.55, 41.0, 32.4, 30.0, 29.9, 28.6, 27.8, 23.3, 14.5; one peak is missing due to overlap. Characterization in accordance with data reported in the literature.[10]

***N*-2-(2-(2-ethoxy)ethoxy)ethanol-3,4-*peri*-Xanthenoxanthene-dicarboxylic-imide 2^{Teg}, PXXMI.** In a single-neck round bottom flask, compound **21^{Teg}** (70.0 mg, 0.14 mmol), pivalic acid (29.3 mg, 0.28 mmol) and CuI (82.0 mg, 0.43 mmol) were dissolved in DMSO (4 mL). The reaction mixture was heated at 150 °C under air for 5 hours. The resulting mixture was poured into H_2O and extracted with $CHCl_3$. The combined organic layers combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude material was precipitated in petroleum ether and filtered over a Millipore filter (PTFE, 0.44 µm) affording *title compound* **2^{Teg}** as a red solid (40 mg, 58%). M.p.: 220 – 224 °C. FTIR (ATR) ν (cm^{-1}): 3449, 2916, 2864, 1688, 1659, 1641, 1597, 1506, 1437, 1396, 1342, 1314, 1273, 1246, 1098, 1055, 1022, 943, 822, 810, 756, 739, 714, 652, 598, 584, 503, 446, 422. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.91 (d, 1H, *J* = 8.3 Hz), 7.44 (s, 1H), 7.20 (d, 1H, *J* = 9.1 Hz), 7.02 – 6.90 (m, 2H), 6.74 (d, 1H, *J* = 9.1 Hz), 6.61 (d, 1H, *J* = 8.3 Hz), 6.41 (d, 1H, *J* = 7.3 Hz), 4.26 (t, 2H, *J* = 5.4 Hz), 3.80 (t, 2H, *J* = 5.4 Hz), 3.72 – 3.49 (m, 8H), 2.86 (br, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 163.0, 162.8, 156.6, 151.7, 144.9, 144.7, 133.3, 131.2, 129.3, 128.3, 125.9, 120.7, 120.6, 120.2, 120.2, 118.2, 118.0, 117.1, 115.2, 110.2, 109.7, 72.7, 70.7, 70.2, 68.2, 61.9, 39.3; one aromatic peak is missing probably due to overlap. HRMS (APCI-TOF): (m/z) $[M + H]^+$ Calcd for $C_{28}H_{22}NO_7$ 484.1396; Found 484.1397.

***N*-mesityl-3,4-*peri*-xanthenoxanthene-dicarboxylic-imide 2^{Mes}, PXXMI.** In a single-neck round bottom flask, compound **21^{Mes}** (70.0 mg, 0.14 mmol), pivalic acid (29.3 mg, 0.28 mmol) and CuI (82.0 mg, 0.43 mmol) were dissolved in DMSO (4 mL). The reaction mixture was heated at 150 °C under air for 5 hours. The resulting mixture was poured into H_2O and extracted with $CHCl_3$. The combined organic layers combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: CH_2Cl_2) to give *title compound* **2^{Mes}** as a red solid (64.5 mg, 93%). M.p.: > 300 °C. FTIR (ATR) ν (cm^{-1}): 2916, 2848, 1697, 1661, 1651, 1595, 1406, 1396, 1381, 1317, 1273, 1248, 1229, 1171, 1128, 1117, 1086, 1069, 1057, 1034, 826, 812, 791, 741, 836, 496, 457. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.34 (d, 1H, *J* = 8.3 Hz), 8.03 (s, 1H), 7.53 (d, 1H, *J* = 9.2 Hz), 7.22 – 7.18 (m, 2H), 7.12 (d, 1H, *J* = 9.2 Hz), 7.03 – 6.99 (m, 3H), 6.78 (dd, 1H, *J* = 6.3, 2.0 Hz), 2.35 (s, 3H), 2.09 (s, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 162.9, 162.6, 157.5, 152.3, 145.4, 145.3, 138.5, 135.1, 134.1, 131.7, 131.6, 129.6, 129.5,

128.5, 127.3, 121.3, 121.3, 121.0, 120.9, 119.3, 119.1, 117.5, 115.9, 110.4, 110.4, 21.3, 18.0; one peak is missing probably due to overlap. HRMS (APCI-TOF): (m/z) $[M + H]^+$ Calcd for $C_{31}H_{20}NO_4$ 470.1392; Found 470.1393.

2,5,8-tri-tert-butyl-11-methoxyperylene 26. To a stirred mixture of compound 5,8,11-tri-*tert*-butylperylen-2-ol **25** (500 mg, 1.14 mmol) and K_2CO_3 (625 mg, 4.52 mmol) in anhydrous acetone (6 mL) at 60 °C under N_2, MeI (0.27 mL, 4.52 mmol) was added, and the mixture stirred overnight at 50 °C under N_2. After cooling down to r.t., the solvent was removed *in vacuo* and the residue taken in CH_2Cl_2 and washed with H_2O (×3) and brine. The organic layer was dried over Na_2SO_4 and the solvent evaporated under reduced pressure. The reaction crude was purified by silica column chromatography (eluents: petroleum ether:EtOAc, 100:2) to afford compound *title compound* **26** (445 mg, 87%) as a yellow solid. M.p.: 271 – 273 °C. FTIR (ATR) *ν* (cm^{-1}): 2949, 2903, 1603, 1387, 1358, 1335, 1290, 1259, 1236, 1217, 1200, 1167, 1155, 1111, 1074, 1041, 953, 914, 876, 866, 856, 820, 781, 723, 669, 660, 642, 623, 582, 534, 436, 424, 418, 409. ^1H NMR (CD_2Cl_2, 400 MHz): *δ* 8.27 (d, 1H, *J* = 2.0 Hz), 8.22 (d, 1H, *J* = 2.0 Hz), 8.19 (d, 1H, *J* = 1.6 Hz), 7.82 (d, 1H, *J* = 2.4 Hz), 7.67 (d, 1H, *J* = 1.6 Hz), 7.66 (d, 1H, *J* = 1.6 Hz), 7.59 (d, 1H, *J* = 1.6 Hz), 7.05 (d, 1H, *J* = 2.4 Hz), 3.96 (s, 3H), 1.49 (s, 18H), 1.47 (s, 9H). ^{13}C NMR (CD_2Cl_2, 100 MHz): *δ* 158.7, 150.1, 149.53, 149.49, 136.9, 135.3, 133.3, 131.3, 130.9, 130.3, 125.9, 124.4, 124.0, 123.5, 123.0, 119.2, 118.7, 117.0, 111.8, 106.6, 55.8, 35.4, 31.6, 31.6; some aliphatic peaks are missing probably due to overlap. HRMS (ESI): m/z $[M + H]^+$, Calcd for $C_{33}H_{39}O$ 451.3001; Found 451.2999.

3-bromo-5,8,11-tri-tert-butyl-2-methoxyperylene 27. Perylene derivative **26** (50.0 mg, 0.11 mmol) was dissolved into $CHCl_3$ (3 mL) and the solution cooled to 0 °C. NBS (20.0 mg, 0.11 mmol) was thus added and the resulted mixture stirred at 0 °C for 20 minutes. The reaction was quenched with H_2O and extracted with CH_2Cl_2. The organic layer was additionally washed with H_2O (×2) and dried over Na_2SO_4. The solvent was removed under reduced pressure to yield *title compound* **27** as a brown solid (57 mg, quantitative). M.p.: 205 – 212 °C. FTIR (ATR) *ν* (cm^{-1}): 2961, 2864, 1591, 1510, 1462, 1448, 1429, 1393, 1369, 1362, 1344, 1327, 1258, 1242, 1200, 1113, 1094, 1063, 1047, 987, 970, 922, 878, 870, 837, 781, 731, 677, 662, 633, 615, 556, 509, 417. ^1H NMR (CD_2Cl_2, 400 MHz): *δ* 8.32 (d, 1H, *J* = 1.7 Hz), 8.27 (d, 1H, *J* = 1.7 Hz), 8.24 (d, 1H, *J* = 1.7 Hz), 8.08 (d, 1H, *J* = 1.7 Hz), 7.92 (s, 1H), 7.72 (d, 1H, *J* = 1.6 Hz), 7.70 (d, 1H, *J* = 1.6 Hz), 4.13 (s, 3H), 1.52 (s, 9H), 1.49 (s, 18H). ^{13}C NMR (CD_2Cl_2, 100 MHz): *δ* 155.0, 151.4, 149.8, 149.6, 135.3, 134.9, 132.7, 131.7, 130.5, 129.9, 125.5, 125.0, 124.6, 124.4, 122.2, 119.3, 119.1, 117.9, 109.5, 107.1, 57.6, 35.8, 35.4, 31.6, 31.5; some aliphatic peaks are missing probably due to overlap. HRMS (ESI): m/z $[M]^+$ Calcd for $C_{33}H_{37}OBr$ 528.2028; Found 528.2051.

Dimethyl 3-methoxy-4-(5,8,11-tri-tert-butyl-2-methoxyperylen-3-yl)naphthalene-1,8-dicarboxylate 22. In a 50 mL two-neck round bottom flask, compound **27** (100 mg, 0.19 mmol) and K_3PO_4 (163 mg, 0.77 mmol) were dissolved in 1,4-dioxane (10 mL) and H_2O (4 drops) and the reaction mixture degassed by bubbling N_2 under sonication for 20 minutes. $[Pd(dba)_2]$ (5.40 mg, 9.40 µmol), SPhos (7.70 mg, 18.8 µmol) and compound **7** (151 mg, 0.38 mmol) were thus added under N_2 and the reaction mixture degassed for additional 20 minutes. The reaction was refluxed under N_2 for 20 hours. After cooling down to r.t., the mixture was filtered over celite® and washed abundantly with CH_2Cl_2 and EtOAc. The solvents were removed under reduced pressure and the crude purified by silica column chromatography (eluents: petroleum ether:EtOAc 90:10 to 85:15) to afford *title compound* **22** as a yellow solid (80 mg, 59%). M.p.: 148 – 155 °C. FTIR (ATR) *ν* (cm^{-1}): 2953, 2907, 2868, 1720, 1601, 1585, 1508, 1460, 1433, 1342, 1267, 1231, 1167, 1151, 1132, 1090, 1070, 1022, 972, 926, 867, 768, 727, 638, 413. ^1H NMR (CD_2Cl_2, 400 MHz): *δ* 8.31 (m, 2H), 8.21 (d, 1H, *J* = 1.6 Hz), 8.07 (s, 1H), 7.97 (s, 1H), 7.83 (dd, 1H, *J* = 7.2, 1.2 Hz), 7.73 (d, 1H, *J* = 1.6 Hz), 7.71 (d, 1H, *J* = 1.6 Hz), 7.51 – 7.49 (dd, 1H, *J* = 8.8, 1.2 Hz), 7.30 (dd, 1H, *J* = 8.8, 7.2 Hz), 6.90 (d, 1H, *J* = 1.6 Hz), 3.96 (s, 3H), 3.93 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H), 1.53 (s, 9H), 1.50 (s, 9H), 1.20 (s, 9H). ^{13}C NMR (CD_2Cl_2, 125 MHz): *δ* 169.9, 169.5, 156.2, 154.8, 150.3, 149.7, 149.6, 135.8, 135.6, 135.4, 133.7, 131.6, 131.5, 131.0, 130.51, 130.45, 130.4, 128.5, 126.1, 125.8, 124.7, 124.6, 124.2, 123.8, 123.6, 121.0, 119.00, 118.95, 118.9, 118.2, 117.3, 107.0, 57.3, 57.1, 52.7, 52.6 35.43, 35.41, 35.3, 31.62, 31.61, 31.3. HRMS (ESI): m/z $[M + H]^+$ Calcd for $C_{48}H_{51}O_6$ 723.3686; Found 723.3674.

5-methoxy-2-octyl-6-(5,8,11-tri-tert-butyl-2-methoxyperylen-3-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 23. Compound **22** (78.0 mg, 0.10 mmol) and KOH (13.0 mg, 0.23 mmol) were dissolved in *i*PrOH (2 mL) and refluxed for 13 hours. After cooling down to r.t., the reaction was quenched with 1M HCl and the so formed precipitate separated by centrifugation. The collected orange solid was dissolved in 1,4-dioxane (3 mL) and DIPEA (50.0 µL, 0.2929 mmol) and *n*-octylamine (22.0 µL, 0.13 mmol) were added. The reaction mixture was refluxed for 20 hours. After cooling down to r.t., H_2O was added to the reaction mixture and the aqueous phase extracted with CH_2Cl_2 (×3). Combined organic layers were dried over Na_2SO_4 and the solvent removed *in vacuo*. Purification of the crude through silica column chromatography (eluents: petroleum ether:EtOAc 9:1) yielded *title compound* **23** (62 mg, 73 %) as an orange solid. M.p.: 139 – 140 °C. FTIR (ATR) *ν* (cm^{-1}): 2953, 2853, 1699, 1659, 1593, 1512, 1462, 1404, 1360, 1342, 1327, 1277, 1256, 1180, 1148, 1088, 1053, 1038, 972, 872, 845, 783, 746, 725, 636, 592. ^1H NMR (CD_2Cl_2, 400 MHz): *δ* 8.54 (s, 1H), 8.43 (dd, 1H, *J* = 7.2, 1.2 Hz), 8.34 – 8.31 (m, 2H), 8.21 (d, 1H, *J* = 1.7 Hz), 8.09 (s, 1H), 7.75 (d, 1H, *J* = 1.6 Hz), 7.72 (d, 1H, *J* = 1.6 Hz), 7.66 (dd, 1H, *J* = 8.6, 1.2 Hz), 7.51 (dd, 1H, *J* = 8.6, 7.2 Hz), 6.86 (d, 1H, *J* = 1.7 Hz), 4.24 – 4.17 (m, 2H), 3.96 (s, 3H), 3.87 (s, 3H), 1.77 (m, 2H), 1.52 (s, 9H), 1.51 (s, 9H), 1.38 – 1.24 (m, 10H), 1.18 (s, 9H), 0.90 (t, 3H, *J* = 6.8 Hz). ^{13}C NMR (CD_2Cl_2, 100 MHz): *δ* 164.7, 164.6, 156.5, 156.1, 150.4, 149.7, 149.6, 135.42, 135.36, 134.0, 133.3, 132.3, 131.6, 130.8, 130.4, 129.3, 127.70, 127.65, 125.8, 124.8, 124.5, 124.30, 124.26, 123.7, 123.5, 120.7, 119.1, 119.0, 118.0, 117.5, 117.3, 106.8, 57.4, 57.1, 41.0, 35.41, 35.40, 35.3, 32.4, 31.60, 31.59, 31.3, 30.0, 29.8, 28.7, 27.8, 23.2, 14.4. HRMS (ESI): m/z $[M + H]^+$ Calcd for $C_{54}H_{62}NO_4$ 788.4679; Found 788.4673.

5-hydroxy-2-octyl-6-(5,8,11-tri-tert-butyl-2-hydroxyperylen-3-yl)-1*H*-benzo[*de*]isoquinoline-1,3(2*H*)-dione 24. In a flame dried Schlenk tube, dimethoxy derivative **23** (50.0 mg, 0.06 mmol) and NaOH (15.0 mg, 0.38 mmol) were dissolved in anhydrous NMP (1 mL). 1-Decanethiol (16.04 µL, 0.19 mmol) was thus added and the reaction mixture stirred at 130 °C for 4 hours under N_2 atmosphere. After cooling down to r.t., CH_2Cl_2 was added to the mixture and the organic solution washed with 1M HCl (×1), H_2O (×2) and brine (×2). The organic layer was dried over Na_2SO_4 and the solvent removed *in vacuo*. The crude was purified by silica column chromatography (eluents: petroleum ether:EtOAc 9:1 to 8:2) to afford *title compound* **24** (45 mg, 94%) as orange solid when evaporated from MeOH. The compound is sensitive to air and light. M.p.: 114 – 120 °C. FTIR (ATR) ν (cm^{-1}): 3341, 2953, 2920, 2851, 1697, 1649, 1599, 1516, 1462, 1408, 1367, 1337, 1256, 1022, 878, 808, 785, 746, 635, 575, 403. ^{1}H NMR ($(CD_3)_2CO$, 400 MHz): two O*H* peaks are missing, δ 8.51 (d, 1H, J = 2 Hz), 8.43 (d, 1H, J = 1.6 Hz), 8.38 – 8.36 (m, 3H), 8.19 (s, 1H), 7.84 (d, 1H, J = 1.6 Hz), 7.81 (d, 1H, J = 1.6 Hz), 7.70 (dd, 1H, J = 8.4, 1.2 Hz), 7.62 (dd, 1H, J = 8.4, 7.2 Hz), 7.01 (d, 1H, J = 1.6 Hz), 4.21 – 4.16 (m, 2H), 1.81 – 1.74 (m, 2H), 1.52 (s, 9H), 1.50 (s, 9H), 1.32 – 1.28 (m, 10H), 1.18 (s, 9H), 0.89 (t, 3H, J = 6.8 Hz). ^{13}C NMR ($(CD_3)_2CO$, 150 MHz): δ 164.8, 164.4, 155.6, 155.2, 150.6, 150.1, 150.0, 136.6, 136.0, 134.4, 134.3, 132.2, 132.1, 131.5, 130.8, 128.5, 128.1, 126.2, 125.1, 124.9, 124.7, 124.6, 123.9, 123.8, 123.1, 121.0, 119.5, 117.1, 114.3, 112.2, 40.9, 35.7, 35.5, 32.6, 31.6, 31.4, 28.9, 28.0, 23.4, 14.4; two aromatic and four aliphatic peaks are missing probably due to overlap. HRMS (ESI): m/z $[M + H]^+$ Calcd for $C_{52}H_{58}NO_4$ 760.4366; Found 760.4366.

***N*-octyl *peri*-π-extended PXXMI 2^{Per}.** In a 10 mL round bottom flask, dihydroxy derivative **24** (37.0 mg, 0.05 mmol), CuI (27.4 mg, 0.14 mmol) and pivalic acid (9.80 mg, 0.10 mmol) were dissolved in DMSO (1.5 mL). The reaction mixture was stirred at 150 °C under air and monitored by TLC. After 3 hours the reaction turned from yellow to dark violet and complete conversion of the starting material was detected. After cooling down to r.t., the reaction mixture was diluted with CH_2Cl_2 (10 mL) and the organic layer washed abundantly with sat. aq. NH_4OH (until the aq. phase resulted to be colorless), H_2O (×2) and brine (×1). The organic layer was separated, and the solvent removed under reduced pressure (the organic phase was not dried over a drying agent in order to limit the loss of compound due to the low solubility of **2^{Per}** in commonly used organic solvents). The reaction crude was purified by precipitation from THF/MeOH (until the supernatant resulted colorless) to give *title compound* **2^{Per}** (24 mg, 65%) as dark violet solid. M.p.: > 300 °C. FTIR (ATR) ν (cm^{-1}): 2949, 2918, 2853, 1686, 1661, 1643, 1622, 1593, 1483, 1458, 1431, 1406, 1385, 1369, 1348, 1327, 1286, 1273, 1242, 1205, 1188, 1124, 1090, 1036, 1016, 937, 903, 874, 852, 826, 812, 804, 789, 760, 748, 716, 700, 633, 619, 598, 557, 552, 415, 403. ^{1}H NMR ($C_2D_2Cl_4$, 600 MHz): δ 8.02 (br, 1H), 7.95 (br, 1H), 7.83 (br, 1H), 7.71 – 7.48 (m, 2H), 7.46 (br, 1H), 7.33 (br, 1H), 6.82 (br, 1H), 4.09 – 4.01 (m, 2H), 1.78 – 1.66 (m, 10H), 1.54 – 1.26 (m, 22H), 0.92 (t, 3H, J = 6.5 Hz). Seven aliphatic protons are missing probably due to overlap with the H_2O peak of the deuterated solvent at 1.61 ppm. HRMS (MALDI): m/z $[M]^+$ Calcd for $C_{52}H_{53}NO_4$ 755.3975; Found 755.3975.

▪ ASSOCIATED CONTENT

Supporting Information

Synthesis schemes, ^{1}H and ^{13}C NMR spectra of isolated compounds, photophysical characterization data, and AFM images (PDF).

The Supporting Information is available free of charge on the ACS Publications website.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

None

ACKNOWLEDGMENT

D.B. gratefully acknowledges the EU through the MSCA-ITN ETN network "PHOTOTRAIN", the MSCA-RISE project "INFUSION" and Cardiff University.

▪ REFERENCES

(1) (a) Wang, L.; Duan, G.; Ji, Y.; Zhang, H. Electronic and Charge Transport Properties of peri-Xanthenoxanthene: The Effects of Heteroatoms and Phenyl Substitutions. *J. Phys. Chem. C* **2012**, *116*, 22679-22686. (b) Shukla, D.; Welter, T. R.; Robello, D. R.; Giesen, D. J.; Lenhard, J. R.; Ahearn, W. G.; Meyer, D. M.; Rajeswaran, M. Dioxapyrene-Based Organic Semiconductors for Organic Field Effect Transistors. *J. Phys. Chem. C* **2009**, *113*, 14482-14486. (c) Wu, D.; Pisula, W.; Haberecht, M. C.; Feng, X.; Müllen, K. Oxygen- and Sulfur-Containing Positively Charged Polycyclic Aromatic Hydrocarbons. *Org. Lett.* **2009**, *11*, 5686-5689. (d) Nakahara, K.; Mitsui, C.; Okamoto, T.; Yamagishi, M.; Matsui, H.; Ueno, T.; Tanaka, Y.; Yano, M.; Matsushita, T.; Soeda, J.; Hirose, Y.; Sato, H.; Yamano, A.; Takeya, J. Furan Fused V-Shaped Organic Semiconducting Materials with High Emission and High Mobility. *Chem. Commun.* **2014**, *50*, 5342-5344. (e) Nakanishi, K.; Fukatsu, D.; Takaishi, K.; Tsuji, T.; Uenaka, K.; Kuramochi, K.; Kawabata, T.; Tsubaki, K. Oligonaphthofurans: Fan-Shaped and Three-Dimensional π-Compounds. *J. Am. Chem. Soc.* **2014**, *136*, 7101-7109. (f) Yang, L.; Li, M.; Song, J.; Zhou, Y.; Bo, Z.; Wang, H. Molecular Consideration for Small Molecular Acceptors Based on Ladder-Type Dipyran: Influences of O-Functionalization and π-Bridges. *Adv. Funct. Mater.* **2018**, *28*, 1705927. (g) Zhou, Y.; Li, M.; Song, J.; Liu, Y.; Zhang, J.; Yang, L.; Zhang, Z.; Bo, Z.; Wang, H. High Efficiency Small Molecular Acceptors Based on Novel O-Functionalized Ladder-Type Dipyran Building Block. *Nano Energy* **2018**, *45*, 10-20. (h) Li, M.; Guo, Y.; Zhou, Y.; Zhang, J.; Yang, L.; Zhang, L.; Song, J.; Bo, Z.; Wang, H. Facile Synthesis of the O-

Functionalized Ladder-Type Dipyran Building Block and Its Application in Polymer Solar Cells. *ACS Appl. Mater. Interfaces* **2018**, *10*, 13931-13940.
(2) (a) Pummerer, R.; Prell, E.; Rieche, A. Preparation of Binaphthylene Dioxide. *Ber. Dtsch. Chem. Ges. B* **1926**, *59*, 2159-2161. (b) Pummerer, R.; Rieche, A. Oxidation of Phenols. IX. Aromatic Peroxides and Univalent Oxygen. *Ber. Dtsch. Chem. Ges. B* **1926**, *59*, 2161-2175.
(3) (a) Kobayashi, N.; Sasaki, M. Dioxaanthanthrene Compound and Semiconductor Device. US20090289248A1, 2009. (b) Kobayashi, N.; Sasaki, M.; Nomoto, K. Stable peri-Xanthenoxanthene Thin-Film Transistors with Efficient Carrier Injection. *Chem. Mater.* **2009**, *21*, 552-556. (c) Yoneya, N.; Ono, H.; Ishii, Y.; Himori, K.; Hirai, N.; Abe, H.; Yumoto, A.; Kobayashi, N.; Nomoto, K. Flexible Electrophoretic Display Driven by Solution-Processed Organic Thin-Film Transistors. *J. Soc. Inf. Disp.* **2012**, *20*, 143-147.
(4) (a) Christensen, J. A.; Zhang, J.; Zhou, J.; Nelson, J. N.; Wasielewski, R. Near-Infrared Excitation of the peri-Xanthenoxanthene Radical Cation Drives Energy-Demanding Hole Transfer Reactions. *J. Phys. Chem. C* **2018**, DOI: 10.1021/acs.jpcc.8b07819. (b) Kamei, T.; Uryu, M.; Shimada, T. Cu-Catalyzed Aerobic Oxidative C-H/C-O Cyclization of 2,2'-Binaphthols: Practical Synthesis of PXX Derivatives. *Org. Lett.* **2017**, *19*, 2714-2717. (c) Lv, N.; Xie, M.; Gu, W.; Ruan, H.; Qiu, S.; Zhou, C.; Cui, Z. Synthesis, Properties, and Structures of Functionalized peri-Xanthenoxanthene. *Org. Lett.* **2013**, *15*, 2382-2385. (d) Rasmusson, T.; Martyn, L. J. P.; Chen, G.; Lough, A.; Oh, M.; Yudin, A. K. Aromatic Fluorine as a Versatile Control Element for the Construction of Molecules with Helical Chirality. *Angew. Chem., Int. Ed.* **2008**, *47*, 7009-7012.
(5) Stassen, D.; Demitri, N.; Bonifazi, D. Extended O-Doped Polycyclic Aromatic Hydrocarbons. *Angew. Chem., Int. Ed.* **2016**, 55, 5947-5951.
(6) Berezin, A.; Biot, N.; Battisti, T.; Bonifazi, D. Oxygen-Doped Zig-Zag Molecular Ribbons. *Angew. Chem., Int. Ed.* **2018**, 57, 8942-8946.
(7) Miletić, T.; Fermi, A.; Orfanos, I.; Avramopoulos, A.; De Leo, F.; Demitri, N.; Bergamini, G.; Ceroni, P.; Papadopoulos, M. G.; Couris, S.; Bonifazi, D. Tailoring Colors by O Annulation of Polycyclic Aromatic Hydrocarbons. *Chem. Eur. J.* **2017**, *23*, 2363-2378.
(8) (a) Sakai, N.; Mareda, J.; Vauthey, E.; Matile, S. Core-Substituted Naphthalenediimides. *Chem. Commun.* **2010**, *46*, 4225-4237. (b) Suraru, S.-L.; Würthner, F. Strategies for the Synthesis of Functional Naphthalene Diimides. *Angew. Chem., Int. Ed.* **2014**, *53*, 7428-7448. (c) Kobaisi, M. A.; Bhosale, S. V.; Latham, K.; Raynor, A. M.; Bhosale, S. V. Functional Naphthalene Diimides: Synthesis, Properties, and Applications. *Chem. Rev.* **2016**, *116*, 11685-11796.
(9) (a) Bullock, J. E.; Vagnini, M. T.; Ramanan, C.; Co, D. T.; Wilson, T. M.; Dicke, J. W.; Marks, T. J.; Wasielewski, M. R. Photophysics and Redox Properties of Rylene Imide and Diimide Dyes Alkylated Ortho to the Imide Groups. *J. Phys. Chem. B* **2010**, *114*, 1794-1802. (b) Würthner, F.; Saha-Moeller, C. R.; Fimmel, B.; Ogi, S.; Leowanawat, P.; Schmidt, D. Perylene Bisimide Dye Assemblies as Archetype Functional Supramolecular Materials. *Chem. Rev.* **2016**, *116*, 962-1052. For AB-type PDIS see (c) Schwartz, P.-O.; Biniek, L. Zaborova, E.; Heinrich, B.; Brinkmann, M.; Leclerc, N.; Méry, S. Perylenediimide-Based Donor–Acceptor Dyads and Triads: Impact of Molecular Architecture on Self-Assembling Properties. *J. Am. Chem. Soc.,* **2014**, *136*, 5981-5992 and (d) Peng, J.; Zhai, F.; Guo, X.; Jiang, X.; Ma, Y. Self-assembly and Phase Separation of Amphiphilic Dyads Based on 4,7-bis(2-thienyl)Benzothiodiazole and Perylene Diimide. *RSC Adv.,* **2014**, *4*, 13078-13084.
(10) Sciutto, A.; Fermi, A.; Folli, A.; Battisti, T.; Beames, J. M.; Murphy, D. M.; Bonifazi, D. Customizing Photoredox Properties of PXX-based Dyes through Energy Level Rigid Shifts of Frontier Molecular Orbitals. *Chem. Eur. J.* **2018**, *24*, 4382-4389.
(11) Bollweg, B.; Zeh, L.; Kramer, E. Dinaphthylene Dioxide Derivatives. DE545212, 1932.
(12) Kamei, T.; Takamatsu, Y.; Takenaka, N. Preparation of peri-Xanthenoxanthene Bisimide Compound, its Manufacturing Method, an Organic el Device and an Organic Thin Film Solar Cell JP2018039777 A 20180315, 2018.
(13) Kelber, J.; Achard, M.-F.; Durola, F.; Bock, H. Distorted Arene Core Allows Room-Temperature Columnar Liquid-Crystal Glass with Minimal Side Chains. *Angew. Chem., Int. Ed.* **2012**, *51*, 5200-5203.
(14) Bhatt, M. V.; Kulkarni, S. U. Cleavage of Ethers. *Synthesis* **1983**, 249-282.
(15) (a) Berezin, A. A.; Sciutto, A.; Demitri, N.; Bonifazi, D. Rational Synthesis of AB-Type N-Substituted Core-Functionalized Naphthalene Diimides (cNDIs). *Org. Lett.* **2015**, *17*, 1870-1873. (b) Rocard, L.; Berezin, A.; De Leo, F.; Bonifazi, D. Templated Chromophore Assembly by Dynamic Covalent Bonds. *Angew. Chem., Int. Ed.* **2015**, 54, 15739-15743.
(16) Würth, C.; Grabolle, M.; Pauli, J.; Spieles, M.; Resch-Genger, U. Relative and Absolute Determination of Fluorescence Quantum Yields of Transparent Samples. *Nat. Protoc.* **2013**, *8*, 1535-1550.
(17) Chen, Z.; Fimmel, B.; Würthner, F. Solvent and Substituent Effects on Aggregation Constants of Perylene Bisimide π-Stacks – a Linear Free Energy Relationship Analysis. *Org. Biomol. Chem.* **2012**, *10*, 5845-5855.
(18) Oura, K., Lifshits, V.G., Saranin, A., Zotov, A.V., Katayama, M. In *Surface Science: An Introduction*. Springer-Verlag: Berlin Heidelberg, 2003.
(19) (a) De Luca, G.; Liscio, A.; Maccagnani, P.; Nolde, F.; Palermo, V.; Müllen, K.; Samori, P. Nucleation-governed Reversible Self-assembly of an Organic Semiconductor at Surfaces: Long-range Mass Transport Forming Giant Functional Fibers. *Adv. Funct. Mater.* **2007**, *17*, 3791-3798. (b) De Luca, G.; Liscio, A.; Nolde, F.; Scolaro, L. M.; Palermo, V.; Müllen, K.; Samori, P. Self-assembly of Discotic Molecules into Mesoscopic Crystals by Solvent-vapor Annealing. *Soft Matter* **2008**, *4*, 2064-2070.
(20) Crosby, G. A.; Demas, J. N. Measurement of photoluminescence quantum yields. Review. *J. Phys. Chem.* **1971**, *75*, 991-1024.
(21) Vyskočil, Š.; Meca, L.; Tišlerová, I.; Císařová, I.; Polášek, M.; Harutyunyan, S. R.; Belokon, Y. N.; Stead, R. M. J.; Farrugia, L.; Lockhart, S. C.; Mitchell, W. L.; Kočovský, P. 2,8′ -Disubstituted-1,1′ -Binaphthyls: A New Pattern in Chiral Ligands. *Chem. Eur. J.* **2002**, *8*, 4633-4648.