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One-Step Synthesis of Unsymmetrical *N*-Alkyl-*N*′-aryl Perylene Diimides

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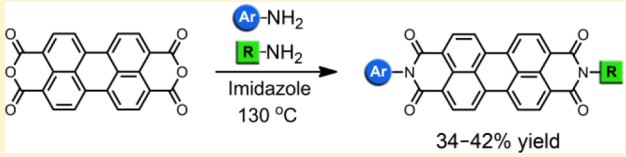
Supporting Information

ABSTRACT: An efficient and facile protocol for the synthesis of unsymmetrical *N*-alkyl-*N*′-aryl perylene diimides is reported that circumvents the need for multiple reaction steps. A number of unsymmetrical perylene diimides containing a solubilizing swallowtail alkyl group and a variety of substituted aryl groups can be prepared in a single step from a simple mixture of amines.

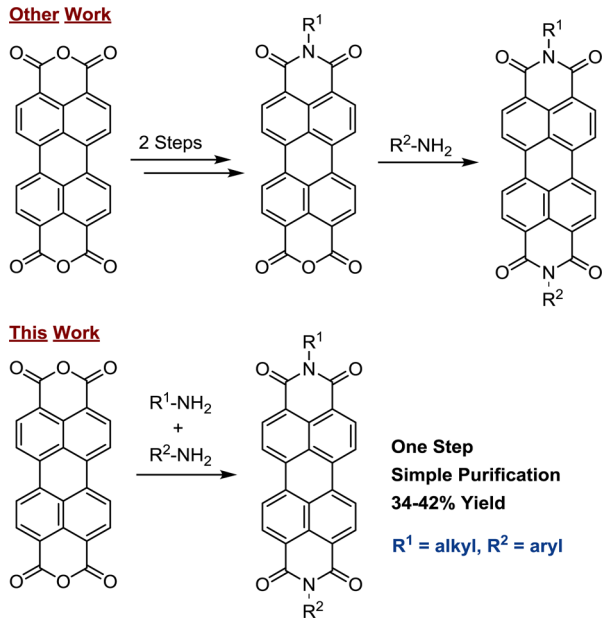


Perylene diimides (PDIs) are a class of materials that have found widespread use in a number of diverse fields. Originally developed as industrial pigments, their outstanding properties including high photochemical stability, fluorescence quantum yields near unity, propensity to self-assemble, and strong electron-accepting character have propelled PDIs toward applications in (multi)chromophoric systems,[1] supramolecular chemistry,[2] and organic electronics.[3]

Unsymmetrical PDIs bearing unique substituents at each imide position constitute an important subgroup within this class of materials due to their significant synthetic versatility. For example, incorporation of an alkyl group at one imide position imparts good solubility, while a unique substituent on the other imide nitrogen can be utilized to direct assembly or as a handle for further derivatization and the construction of more sophisticated structures. For the former, branched "swallowtail" alkyl amines, such as 1-hexylheptyl amine, are routinely employed for their advantageous solubility properties.[4]

Typically, unsymmetrical PDIs are synthesized according to a multistep process (Scheme 1).[5] First, perylene dianhydride is reacted with an alkyl amine of one type, resulting in a symmetrical PDI. In a second step, one of the imides is converted back into an anhydride in a statistical hydrolysis reaction that often proceeds with difficulty. This second step results in an average yield of 44% from bis(1-hexylheptyl)-PDI.[6] In the third and final step, reaction of the perylene monoimide monoanhydride with a second amine affords the unsymmetrical PDI product. Using a less common protocol, a limited number of alkyl/alkyl[7] and aryl/aryl[8] unsymmetrical PDIs have also been prepared in one step from a mixture of amines; however, the reaction is usually reported to be unsuccessful for mixed alkyl/aryl systems. Traditionally, this mixed approach results almost exclusively in the formation of the two symmetrical PDIs due to the difference in reactivity of the amines with perylene dianhydride.[3b] To the best of our knowledge, there are only two reports in the literature of this type of transformation, both of which resulted in the desired unsymmetrical product in ∼10% yield.[9]

Scheme 1. Synthesis of Unsymmetrical PDIs



Recently, we developed a synthetic procedure that facilitates the preparation of unsymmetrical *N*-alkyl-*N*′-aryl PDIs in a single reaction step from a stoichiometric mixture of the corresponding alkyl and aryl amines in ca. 40% yield after purification.[10] Given the significant difference in pK_a (and nucleophilicity) of alkyl versus aryl amines, it is indeed surprising that reasonable yields could be achieved from a simple mixture of reactants. In this note, we examine the scope and utility of this one-step reaction of a mixture of alkyl and aryl amines with perylene dianhydride for the preparation of unsymmetrical PDIs.

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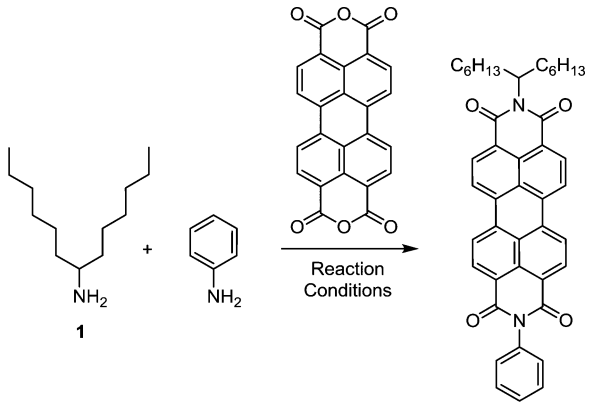
We began by studying the reaction of perylene dianhydride with a mixture of aniline and 1-hexylheptyl amine **1** under a variety of reaction conditions (Table 1). Using imidazole as the solvent at 130 °C, we were pleased to find that the unsymmetrical product was formed and could be readily isolated via silica gel column chromatography in 42% yield. As expected, the bisalkyl PDI is also obtained while the poor solubility of the bisaryl PDI prohibits its isolation. It is also worth noting that imidization proceeded smoothly in the absence of $Zn(OAc)_2$, which is often used as a catalyst. The isolated yield of the unsymmetrical PDI approaches the theoretically expected yield of 50% resulting from a statistical distribution of symmetrical (i.e., alkyl/alkyl, aryl/aryl) and unsymmetrical products. Surprisingly, the same results are achieved when the reaction is performed using 2 equiv of each amine with respect to perylene dianhydride, suggesting a negligible dependence on the nucleophilicity of the amine under these conditions. Conversely, when the reaction is performed using alternative conditions, the yield of the desired unsymmetrical PDI is significantly reduced. For example, the reaction proceeds much more slowly in *N*-methylimidazole (NMI) with the unsymmetrical product being formed in only 27% yield after extended reaction times (Table 1, entry 4). Comparatively, the reaction is accelerated when 4-dimethylaminopyridine (DMAP) is employed; however, the overall yield of the unsymmetrical PDI is approximately the same as with NMI. This disparity is even more apparent when traditional solvents like DMF are employed (Table 1, entry 7), resulting in negligible quantities of the unsymmetrical product and nearly exclusive formation of the symmetrical PDI in accordance with previous literature reports. These findings emphasize the unique efficacy of using imidazole for these imidization reactions.

Table 1. Comparison of Reaction Conditions for the One-Step Synthesis of an Unsymmetrical PDI[a]

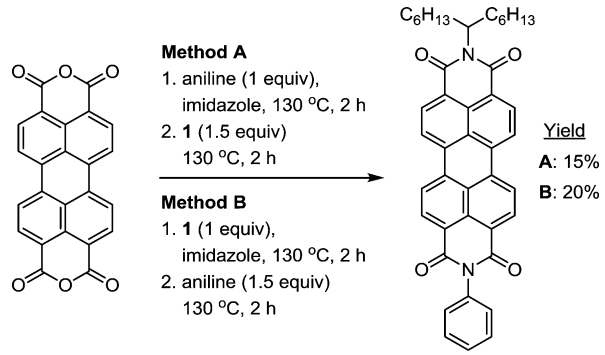


entry	solvent	temp (°C)	reaction time (h)	yield[b] (%)
1	**imidazole**	**130**	**2**	**42**
2[c]	imidazole	130	2	42
3	*N*-methylimidazole	130	2	8
4	*N*-methylimidazole	130	21	27
5	DMAP	130	2	27
6	DMAP	130	7	29
7[d]	DMF	130	3	2

[a]Reaction conditions: 1 equiv of perylene dianhydride, 1 equiv of **1**, 1 equiv of aniline, 60−70 equiv of solvent. [b]Isolated yield after chromatographic separation. [c]With 2 equiv each of **1** and aniline. [d]With 10 equiv of imidazole used.

Based on the results above, the statistical nature of the one-step reaction was investigated in greater detail by performing the reaction in a stepwise fashion (Scheme 2). A similar strategy for the synthesis of unsymmetrical alkyl/aryl PDIs has been reported previously employing several different reaction conditions with mixed results.[11] It is interesting to note that the expected distribution of products resulting from a purely statistical reaction performed in a stepwise fashion is the same as the one-step reaction: alkyl/alkyl (symmetrical, 25%), alkyl/aryl (unsymmetrical, 50%), and aryl/aryl (symmetrical, 25%). In direct contrast to the results obtained using a one-step procedure, we found that the isolated yield of the desired unsymmetrical PDI was significantly reduced to 15−20% when the reaction was performed in a stepwise process (with ∼40% bisalkyl PDI being obtained). Furthermore, the order of amine addition did not influence the outcome of the reaction. Imide formation was also found to be irreversible under the reaction conditions.[12] These results suggest a possible synergistic interaction between the alkyl and aryl amines as well as imidazole that provides a distinct advantage in this single step procedure.

Scheme 2. Stepwise Synthesis of an Unsymmetrical PDI by Sequential Addition of Aniline and Alkyl Amine 1



In order to probe the transformation further, a set of control experiments was performed using 1,8-naphthalic anhydride as a model substrate, and reaction progress was monitored by gas chromatography (Figure 1). A series of reactions were conducted under the standard imidization conditions employed above using a mixture of 1 equiv of each amine with respect to the substrate in imidazole at 130 °C. Remarkably, we found that the phenyl naphthalimide is formed rapidly under these conditions (at ∼50% yield). Moreover, despite ca. 0.5 equiv of remaining aniline, the amount of phenyl naphthalimide does not change over the course of the reaction. In contrast, the alkyl amine reacts relatively slowly, converting the remaining anhydride into the alkyl naphthalimide product over ca. 1 h. Additionally, the rate of formation of the alkyl naphthalimide product was found to be independent of the swallowtail amine concentration. These findings indicate that nucleophilic attack of the amine is not responsible for controlling the rate of imidization. It is important to point out that the phenyl naphthalimide and alkyl naphthalimide products were isolated in excellent yield when the reaction was performed exclusively with either aniline or **1**, respectively. Furthermore, we hypothesized that acid/base equilibria may be important in influencing the extent of reaction observed for the aryl amine.

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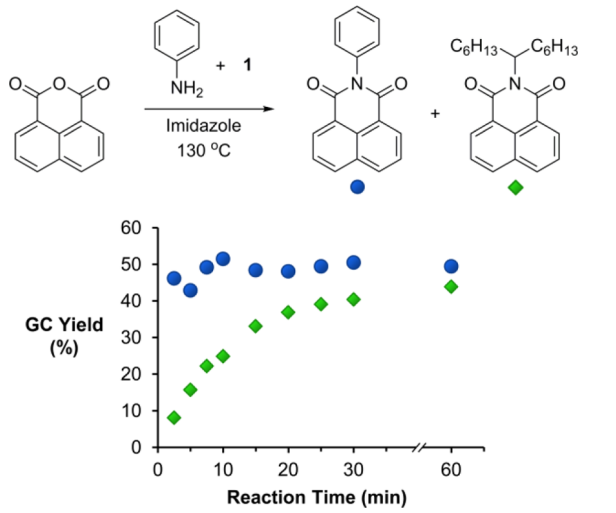


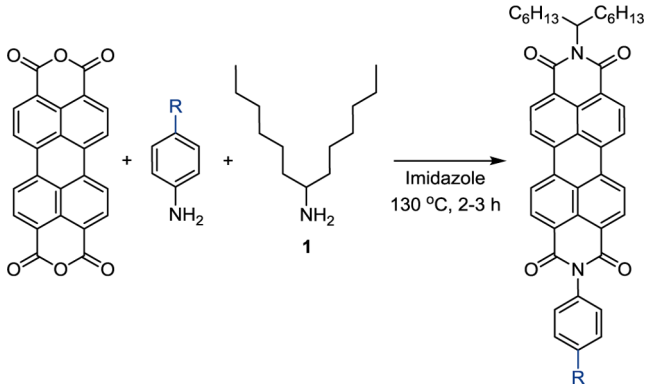
Figure 1. Model reactions performed for varying amounts of time and analyzed by GC demonstrate rapid reaction of aniline and relatively slow reaction of the alkyl amine. The net result is an approximately equal mixture of aryl- and alkyl-substituted products. Reaction conditions: 1.0 equiv of 1,8-naphthalic anhydride, 1.0 equiv of aniline, 1.0 equiv of **1**, 35 equiv of imidazole, 130 °C.

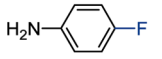
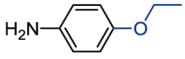
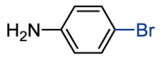
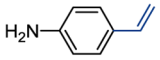
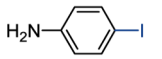
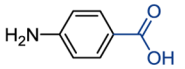
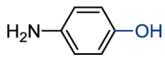
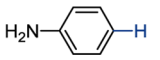
Indeed, the addition of acetic acid or Hünig's base was demonstrated to systematically change the extent of reaction of aniline and the corresponding conversion of the alkyl amine with similar kinetic profiles being observed (see Table S1 in the Supporting Information).

With this information and the successful demonstration of the one-step protocol for the synthesis of unsymmetrical PDIs, we set out to evaluate the scope of this method with a variety of substituted aniline derivatives. This facile one-step procedure was successfully applied to prepare a number of unsymmetrical PDIs using a wide range of aniline starting materials (Table 2). Both electron-rich and electron-deficient anilines were successfully employed, providing similar yields of the unsymmetrical PDIs and demonstrating the robustness of this strategy. Importantly, unsymmetrical PDIs containing diverse functional groups can be prepared in a straightforward fashion allowing for subsequent chemical modification to suit a variety of applications. For example, unsymmetrical PDIs containing aryl halides (Table 2, entries 2 and 3) amenable to Pd-catalyzed cross-coupling reactions and those bearing polymerizable (Table 2, entry 6) as well as nucleophilic or electrophilic groups (Table 2, entries 4 and 7, respectively) are readily accessed. Each of these materials is easily isolated by simple chromatographic techniques in high purity, and the reaction is scalable. To demonstrate the latter point, the unsymmetrical PDI containing an aryl bromide functional group (Table 2, entry 2) was prepared on gram scale.

This one-step protocol for the synthesis of unsymmetrical alkyl/aryl PDIs provides several advantages over the commonly employed multistep procedure. First, the yields for several previously reported PDIs are higher when accessed via the one-step protocol presented here. For example, utilizing **1** and 4-aminobenzoic acid, our method yielded 40% of the desired unsymmetrical product (Table 2, entry 7), while the previously reported synthesis gave only 25% after three steps.[13] Similar overall yields were attained previously for the unsymmetrical PDIs prepared using aniline (28%),[14] 4-iodoaniline (33%),[15] and 4-aminostyrene (14%).[16] In addition to improved yields,

Table 2. One-Step Synthesis of Unsymmetrical PDIs Using a Variety of Substituted Anilines[a]



Entry	Aniline	Yield[b]	Entry	Aniline	Yield[b]
1		42%	5		42%
2		40%	6		36%
3		34%	7[c]		40%
4		39%	8		42%

[a]Reaction conditions: 1.0 equiv of perylene dianhydride, 1.1 equiv of aryl amine, 1.1 equiv of **1**, 70 equiv of imidazole, 130 °C, 2−3 h. [b]Isolated yield (average of two runs). [c]With 1.1 equiv of Hünig's base used.

this one-step method enhances the accessibility of many important unsymmetrical PDI molecules by decreasing both the time and resources required for their preparation.

In conclusion, an efficient and facile protocol for the preparation of unsymmetrical perylene diimides (PDIs) has been successfully demonstrated. Unsymmetrical PDIs containing a swallowtail solubilizing group and aryl substituents with a variety of functional groups can be prepared in a single step from a simple mixture of amines using imidazole as the reaction medium. This protocol provides significant advantages over the traditional three-step methodology commonly employed to access these types of valuable materials.

EXPERIMENTAL SECTION

Materials. All reactions were carried out under an argon atmosphere. All reagents from commercial sources were used without further purification unless otherwise stated. Aniline was fractionally distilled under reduced pressure. The 4-iodoaniline was purified by recrystallization from hexanes. The 1-hexylheptylamine[6b] was prepared according to the literature and purified by vacuum distillation prior to use.

Instrumentation. All compounds were characterized by ^{1}H NMR spectroscopy, IR spectroscopy, and mass spectrometry. Due to the limited solubility of perylene diimides, ^{13}C NMR spectra are reported only for new compounds. Copies of the NMR and mass spectra (FD) can be found in the Supporting Information. NMR spectra were recorded using a 500 or 600 MHz spectrometer. All ^{1}H NMR experiments are reported in δ units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), dichloromethane (5.32 ppm), or tetrahydrofuran (1.73 and 3.58 ppm) in deuterated solvent. All ^{13}C NMR spectra were measured in deuterated solvents and are reported in ppm relative to the signals for

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residual chloroform (77.16 ppm) or tetrahydrofuran (25.37 and 67.57 ppm). Mass spectrometry was performed on a quadrupole/time-of-flight tandem mass spectrometer (ESI) or a time-of-flight mass spectrometer (EI and FD). IR spectra were recorded using an attenuated total reflectance (ATR) sampling accessory. GC analyses were performed using a Restek SHRXI-5MS column (15 m, 0.25 mm i.d.) and FID detector.

General Procedure A. A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with perylene-3,4,9,10-dianhydride, imidazole, and the aryl amine (if a solid). The vessel was sealed with a rubber septum and purged with argon for 5 min. The aryl amine (if a liquid) and 1-hexylheptylamine (d = 0.79 g/mL) were then added via syringe. The contents of the flask were briefly mixed, and the vessel was immersed in an oil bath maintained at 130 °C for the indicated amount of time. At the conclusion of the reaction, the vessel was allowed to cool to room temperature, dichloromethane (DCM) was added (25 mL), and the mixture was briefly sonicated. The mixture was diluted with DCM (100 mL) and washed with aqueous HCl (2M, 100 mL), using a small amount of isopropyl alcohol to break an emulsion if necessary. The aqueous layer was extracted with DCM (2 × 100 mL), and the combined organic fractions were dried over $MgSO_4$, filtered, concentrated with silica gel, and purified by column chromatography.

In all cases, bis(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic diimide (bisalkyl PDI) is the first product to elute from the column ($R_{f,DCM}$ = 0.86), while the second species to elute is the unsymmetrical PDI. The bisalkyl PDI is easily removed by first eluting with 50−100% DCM in hexanes, followed by elution of the unsymmetrical product with a slightly stronger eluent (typically 0−10% EtOAc in DCM).

General Procedure B. General procedure A was used with the following modification: after the vessel was sealed with a rubber septum, *N*,*N*-diisopropylethylamine was added via syringe.

General Procedure C (Stepwise Addition of Amines). A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with perylene-3,4,9,10-dianhydride and imidazole. The vessel was sealed with a rubber septum and purged with argon for 5 min. Either aniline or 1-hexylheptylamine was then added via syringe. The contents of the flask were briefly mixed, and the vessel was immersed in an oil bath maintained at 130 °C. After 2 h, the other amine (either aniline or 1-hexylheptylamine) was added via syringe, and the reaction was continued for another 2 h. At the conclusion of the reaction, the vessel was allowed to cool to room temperature, dichloromethane (DCM) was added (25 mL), and the mixture was briefly sonicated. The mixture was diluted with DCM (100 mL) and washed with aqueous HCl (2 M, 100 mL), using a small amount of isopropyl alcohol to break an emulsion if necessary. The aqueous layer was extracted with DCM (2 × 100 mL), and the combined organic fractions were dried over $MgSO_4$, filtered, concentrated with silica gel, and purified by column chromatography.

General Procedure D. A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with 1,8-naphthalic anhydride and imidazole. The vessel was sealed with a rubber septum and purged with argon for 5 min, followed by the addition of the amine via syringe. The vessel was immersed in an oil bath maintained at 130 °C for the indicated amount of time. At the conclusion of the reaction, the vessel was allowed to cool to room temperature. The contents were dissolved in DCM (100 mL) and washed with aqueous HCl (2 M, 100 mL), using a small amount of isopropyl alcohol to break an emulsion if necessary. The aqueous layer was extracted with DCM (2 × 100 mL), and the combined organic fractions were dried over $MgSO_4$, filtered, concentrated with silica gel, and purified by column chromatography.

General Procedure E (Model Reactions for GC Analysis). A 13 × 100 mm test tube equipped with a magnetic stir bar was charged with 1,8-naphthalic anhydride and imidazole. The tube was sealed with a screw cap containing a Teflon septum, and the vessel was purged with argon for 5 min. Aniline and 1-hexylheptylamine were then added by syringe, and the tube was immersed in an oil bath maintained at 130 °C for the indicated amount of time. At the conclusion of the reaction, the vessel was quickly cooled under a stream of water, dodecane was added as an internal standard, and the contents were dissolved in DCM. The crude reaction mixture was analyzed directly by GC.

General Procedure F. General procedure E was used with the following modification: after the vessel was sealed, either acetic acid or *N*,*N*-diisopropylethylamine was added via syringe.

N-(4-Fluorophenyl)-N′-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic Diimide (Table 2, entry 1). Following general procedure A, a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (392 mg, 0.999 mmol), imidazole (4.7 g, 69 mmol), 4-fluoroaniline (0.10 mL, 1.1 mmol), and 1-hexylheptylamine (0.28 mL, 1.1 mmol) was heated at 130 °C for 2.5 h. The crude product was purified by column chromatography (50−100% DCM/hexanes followed by 0−10% EtOAc/DCM) to provide the title compound as a red solid (310 mg, 46%): R_f = 0.31 (DCM); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 0.84 (t, J = 6.8 Hz, 6H), 1.19−1.38 (m, 16H), 1.84−1.91 (m, 2H), 2.19−2.29 (m, 2H), 5.16 (tt, J = 9.6, 4.3 Hz, 1H), 7.28 (t, J = 8.5 Hz, 2H), 7.34−7.39 (m, 2H), 8.57−8.68 (m, 8H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 22.7, 27.2, 29.4, 31.9, 32.5, 55.1, 116.6 (d, J = 23 Hz), 123.0, 123.1, 123.3, 123.5, 124.3, 126.2, 126.5, 129.4, 129.6, 130.6 (d, J = 8.7 Hz), 130.9 (d, J = 3.3 Hz), 131.0, 131.7, 134.0, 135.0, 162.4 (d, J = 248 Hz), 163.5, 164.4 ppm; IR (solid, cm^{-1}) 3341, 3305, 3099, 2925, 2856, 1697, 1653, 1593, 1341, 1246; HRMS (EI, m/z) calcd for $[C_{43}H_{39}FN_2O_4]^+$ (M^+), 666.2894; found, 666.2900.

N-(4-Bromophenyl)-N′-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic Diimide (Table 2, entry 2). Following general procedure A, a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (1.40 g, 3.57 mmol), imidazole (19 g, 280 mmol), 4-bromoaniline (736 mg, 4.28 mmol), and 1-hexylheptylamine (1.10 mL, 4.35 mmol) was heated at 130 °C for 2 h. The crude product was purified by column chromatography (50−100% DCM/hexanes) to provide the title compound as a red solid (1.01 g, 39%): R_f = 0.43 (DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.83 (t, J = 7.0 Hz, 6H), 1.17−1.38 (m, 16H), 1.82−1.92 (m, 2H), 2.20−2.30 (m, 2H), 5.19 (tt, J = 9.4, J = 5.8 Hz, 1H), 7.23−7.26 (m, 2H), 7.69−7.72 (m, 2H), 8.63−8.76 (m, 8H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 22.7, 27.2, 29.4, 31.9, 32.5, 55.1, 123.1, 123.1, 123.4, 123.6, 124.4, 126.3, 126.6, 129.5, 129.8, 130.6, 131.1, 131.8, 132.8, 134.1, 134.1, 135.2, 163.3, 164.5 ppm; IR (solid, cm^{-1}) 3345, 3309, 2924, 2855, 1698, 1657, 1592, 1340, 1252, 1175; HRMS (ESI, m/z) calcd for $[C_{43}H_{39}BrN_2O_4 + Na]^+$ $(M + Na)^+$, 749.1991; found, 749.1978.

N-(4-Iodophenyl)-N′-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic Diimide (Table 2, entry 3). Following general procedure A, a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (392 mg, 0.999 mmol), imidazole (4.7 g, 69 mmol), 4-iodoaniline (241 mg, 1.10 mmol), and 1-hexylheptylamine (0.28 mL, 1.1 mmol) was heated at 130 °C for 2 h. The crude product was purified by column chromatography (50−100% DCM/hexanes followed by 0−10% EtOAc/DCM) to provide the title compound as a red solid (268 mg, 35%): R_f = 0.47 (DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.83 (t, J = 6.9 Hz, 6H), 1.17−1.40 (m, 16H), 1.83−1.92 (m, 2H), 2.20−2.30 (m, 2H), 5.18 (tt, J = 9.3, 5.9 Hz, 1H), 7.09−7.14 (m, 2H), 7.88−7.93 (m, 2H), 8.61−8.74 (m, 8H) ppm; IR (solid, cm^{-1}) 3345, 3313, 3067, 2953, 2923, 2854, 1697, 1655, 1339, 1251; HRMS (EI, m/z) calcd for $[C_{43}H_{39}IN_2O_4]^+$ (M^+), 774.1955; found, 774.1947.

N-(4-Hydroxyphenyl)-N′-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic Diimide (Table 2, entry 4). Following general procedure A, a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (392 mg, 0.999 mmol), imidazole (4.6 g, 68 mmol), 4-aminophenol (119 mg, 1.09 mmol), and 1-hexylheptylamine (0.27 mL, 1.1 mmol) was heated at 130 °C for 2.75 h. The crude product was purified by column chromatography (50−100% $CHCl_3$/hexanes followed by 0−5% MeOH/$CHCl_3$) followed by precipitation in MeOH. Filtration using a 0.45 μm nylon membrane provided the title compound as a red powder (278 mg, 42%): R_f = 0.26 (95/5 $CHCl_3$/MeOH); ^{1}H NMR (600 MHz, THF-d_8) δ 0.85 (t, J = 7.0 Hz, 6H), 1.20−1.43 (m, 16H), 1.81−1.92 (m, 2H), 2.26−2.37 (m, 2H), 5.19 (tt, J = 9.6, 5.4 Hz, 1H), 6.82−6.89 (m, 2H), 7.11−7.19 (m, 2H), 8.40−8.57 (m, 9H) ppm; ^{13}C NMR (125 MHz, THF-d_8) δ 14.6, 23.7, 28.0, 30.4, 32.9, 33.4, 55.2, 116.2, 116.3, 124.3, 124.4, 125.1, 127.2, 127.3, 128.2, 130.4, 130.5, 130.9, 131.7, 132.2, 135.3, 135.4, 158.6, 164.0 ppm; IR (solid, cm^{-1})

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3415, 3111, 2952, 2924, 2856, 1693, 1655, 1593, 1514, 1344; HRMS (EI, m/z) calcd for $[C_{43}H_{40}N_2O_5]^+$ (M^+), 664.2937; found, 664.2943.

N-(4-Ethoxyphenyl)-N′-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic Diimide (Table 2, entry 5). Following general procedure A, a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (409 mg, 1.04 mmol), imidazole (5.5 g, 81 mmol), 4-ethoxyaniline (0.17 mL, 1.3 mmol), and 1-hexylheptylamine (0.30 mL, 1.2 mmol) was heated at 130 °C for 2 h. The crude product was purified by column chromatography (50−100% DCM/hexanes followed by 0−10% EtOAc/DCM) to provide the title compound as a red solid (295 mg, 41%): R_f = 0.22 (DCM); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 0.84 (t, J = 6.9 Hz, 6H), 1.18−1.39 (m, 16H), 1.47 (t, J = 6.9 Hz, 3H), 1.81−1.90 (m, 2H), 2.19−2.29 (m, 2H), 4.13 (q, J = 6.9 Hz, 2H), 5.17 (tt, J = 9.3, 5.8 Hz, 1H), 7.04−7.10 (m, 2H), 7.22−7.28 (m, 2H), 8.60−8.69 (m, 8H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.2, 15.0, 22.7, 27.1, 29.4, 31.9, 32.5, 55.0, 63.9, 115.4, 123.1, 123.3, 123.5, 124.2, 126.4, 126.6, 127.4, 129.6, 129.6, 129.8, 131.1, 131.8, 131.9, 134.3, 135.0, 159.3, 163.5, 163.8, 164.6 ppm; IR (solid, cm^{-1}) 3349, 3305, 3099, 2656, 2928, 2857, 1694, 1655, 1591, 1246; HRMS (EI, m/z) calcd for $[C_{45}H_{44}N_2O_5]^+$ (M^+), 692.3250; found, 692.3251.

N-(4-Vinylphenyl)-N′-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic Diimide (Table 2, entry 6). Following general procedure A, a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (392 mg, 0.999 mmol), imidazole (4.8 g, 70 mmol), 4-aminostyrene (0.13 mL, 1.1 mmol), and 1-hexylheptylamine (0.28 mL, 1.1 mmol) was heated at 130 °C for 2 h. The crude product was purified by column chromatography (50−100% DCM/hexanes followed by 0−10% EtOAc/DCM) to provide the title compound as a red solid (274 mg, 41%): R_f = 0.37 (DCM); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.83 (t, J = 6.8 Hz, 6H), 1.18−1.39 (m, 16H), 1.83−1.92 (m, 2H), 2.20−2.30 (m, 2H), 5.19 (tt, J = 9.6, 5.9 Hz, 1H), 5.35 (d, J = 11.0 Hz, 1H), 5.84 (d, J = 17.6 Hz, 1H), 6.81 (dd, J = 17.6, 10.9 Hz, 1H), 7.30−7.34 (m, 2H), 7.59−7.63 (m, 2H), 8.64−8.77 (m, 8H) ppm; IR (solid, cm^{-1}) 3345, 3309, 2924, 2856, 1773, 1732, 1697, 1655, 1592, 1341; HRMS (EI, m/z) calcd for $[C_{45}H_{42}N_2O_4]^+$ (M^+), 674.3145; found, 674.3131.

N-(4-Oxycarbonyl)-N′-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic Diimide (Table 2, entry 7). Following general procedure B, a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (385 mg, 0.981 mmol), imidazole (4.7 g, 69 mmol), 4-aminobenzoic acid (148 mg, 1.08 mmol), 1-hexylheptylamine (0.27 mL, 1.1 mmol), and *N,N*-diisopropylethylamine (0.19 mL, 1.1 mmol) was heated at 130 °C for 2.5 h. The crude product was purified by column chromatography (50−100% DCM/hexanes followed by 0−4% AcOH/DCM) followed by precipitation in MeOH. Filtration using a 0.45 μm nylon membrane provided the title compound as a red powder (281 mg, 41%): R_f = 0.43 (95/5 DCM/AcOH); ^{1}H NMR (600 MHz, THF-d_8) δ 0.85 (t, J = 6.8 Hz, 6H), 1.20−1.42 (m, 16H), 1.85−1.92 (m, 2H), 2.27−2.36 (m, 2H), 5.18 (tt, J = 9.2, 4.7 Hz, 1H), 7.54 (d, J = 7.9 Hz, 2H), 8.18 (d, J = 7.9 Hz, 2H), 8.41−8.59 (m, 8H), 11.48 (br s, 1H) ppm; IR (solid, cm^{-1}) 3511, 3076, 2952, 2924, 2855, 1694, 1649, 1592, 1577, 1339; HRMS (EI, m/z) calcd for $[C_{44}H_{40}N_2O_6]^+$ (M^+), 692.2886; found, 692.2869.

N-Phenyl-N′-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic Diimide (Table 2, entry 8). Following general procedure A, a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (393 mg, 1.00 mmol), imidazole (4.8 g, 70 mmol), aniline (0.10 mL, 1.1 mmol), and 1-hexylheptylamine (0.28 mL, 1.1 mmol) was heated at 130 °C for 2 h. The crude product was purified by column chromatography (50−100% DCM/hexanes followed by 0−10% EtOAc/DCM) to provide the title compound as a red solid (265 mg, 41%): R_f = 0.27 (DCM); ^{1}H NMR (600 MHz, CD_2Cl_2) δ 0.84 (t, J = 6.9 Hz, 6H), 1.19−1.38 (m, 16H), 1.81−1.90 (m, 2H), 2.19−2.29 (m, 2H), 5.17 (tt, J = 9.3, 5.7 Hz, 1H), 7.33−7.39 (m, 2H), 7.51−7.55 (m, 1H), 7.56−7.63 (m, 2H), 8.59−8.72 (m, 8H) ppm; IR (solid, cm^{-1}) 3341, 3305, 3101, 3063, 2923, 2855, 1771, 1696, 1653, 1342; HRMS (EI, m/z) calcd for $[C_{43}H_{40}N_2O_4]^+$ (M^+), 648.2988; found, 648.2976.

N-Phenyl-N′-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic Diimide (Stepwise Procedure, Method A). Following general procedure C, a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (429 mg, 1.09 mmol), imidazole (3.5 g, 51 mmol), and aniline (0.10 mL, 1.1 mmol) was heated at 130 °C. After 2 h, 1-hexylheptylamine (0.41 mL, 1.6 mmol) was added via syringe and the reaction was continued for another 2 h. The crude product was purified by column chromatography (50−100% DCM/hexanes followed by 0−10% EtOAc/DCM) to provide the title compound as a red solid (108 mg, 15%). Spectral data were the same as those reported above (Table 2, entry 8).

N-Phenyl-N′-(1-hexylheptyl)perylene-3,4,9,10-tetracarboxylic Diimide (Stepwise Procedure, Method B). Following general procedure C, a mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (413 mg, 1.05 mmol), imidazole (4.1 g, 60 mmol), and 1-hexylheptylamine (0.27 mL, 1.1 mmol) was heated at 130 °C. After 2 h, aniline (0.15 mL, 1.6 mmol) was added via syringe and the reaction was continued for another 2 h. The crude product was purified by column chromatography (50−100% DCM/hexanes followed by 0−10% EtOAc/DCM) to provide the title compound as a red solid (136 mg, 20%). Spectral data were the same as those reported above (Table 2, entry 8).

N-Phenyl-1,8-naphthalimide. Following general procedure D, a mixture of 1,8-naphthalic anhydride (218 mg, 1.10 mmol), imidazole (4.1 g, 60 mmol), and aniline (0.12 mL, 1.3 mmol) was heated at 130 °C for 2.5 h. The crude product was purified by column chromatography (0−60% EtOAc/hexanes) to provide the title compound as a white solid (286 mg, 95%): R_f = 0.35 (30/70 EtOAc/hexanes); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30−7.36 (m, 2H), 7.45−7.52 (m, 1H), 7.52−7.59 (m, 2H), 7.80 (t, J = 7.1 Hz, 2H), 8.28 (dd, J = 8.2, 1.2 Hz, 2H), 8.66 (dd, J = 7.2, 1.2 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 123.0, 127.2, 128.7, 128.8, 128.8, 129.5, 131.7, 131.9, 134.4, 135.6, 164.5 ppm; IR (solid, cm^{-1}) 3355, 3325, 3074, 1698, 1659, 1583, 1499, 1435, 1354, 1234; MS (EI, m/z) calcd for $[C_{18}H_{11}NO_2]^+$ (M^+), 273.08; found, 273.08.

N-(1-Hexylheptyl)-1,8-naphthalimide. Following general procedure D, a mixture of 1,8-naphthalic anhydride (204 mg, 1.03 mmol), imidazole (3.8 g, 56 mmol), and 1-hexylheptylamine (0.31 mL, 1.2 mmol) was heated at 130 °C for 3 h. The crude product was purified by column chromatography (0−20% EtOAc/hexanes) to provide the title compound as a slightly yellow oil (380 mg, 97%): R_f = 0.55 (15/85 EtOAc/hexanes); ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.81 (t, J = 7.0 Hz, 6H), 1.15−1.37 (m, 16H), 1.78−1.86 (m, 2H), 2.18−2.27 (m, 2H), 5.17 (tt, J = 9.5, 5.8 Hz, 1H), 7.75 (t, J = 7.7 Hz, 2H), 8.20 (dd, J = 8.3, 1.2 Hz, 2H), 8.58 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.1, 22.7, 27.0, 29.3, 31.9, 32.5, 54.6, 122.8, 123.5, 127.0, 128.5, 130.9, 131.6, 131.7, 133.6, 164.5, 165.5 ppm; IR (DCM, cm^{-1}) 3349, 3317, 3063, 2924, 2855, 1699, 1657, 1588, 1338, 1237; HRMS (EI, m/z) calcd for $[C_{25}H_{33}NO_2]^+$ (M^+), 379.2511; found, 379.2518.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectral data for all compounds and results of acid/base experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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