

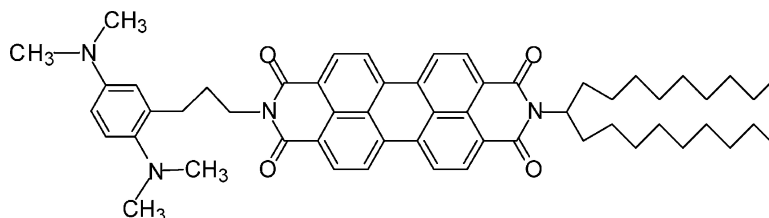
Article

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Donor- σ -Acceptor Molecules Incorporating a Nonadecyl-Swallowtailed Perylenediimide Acceptor

Lyle D. Wescott and Daniell Lewis Mattern*

Department of Chemistry and Biochemistry, University of Mississippi,
Box 1848, University, Mississippi 38677

mattern@olemiss.edu

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Donor- σ -acceptor-lipid molecules were prepared by using perylenetetracarboxylic diimide as the acceptor, starting from perylenetetracarboxylic dianhydride. One imide nitrogen was attached to a "swallowtail" lipid (a long alkyl tail connected at midchain), which imparts enough solubility to make the system tractable and provides a lipophilic region suitable for promoting Langmuir-Blodgett monolayer formation. The other imide link was to a donor group (pyrene, ferrocene, tetramethylphenylenediamine, phenyl) through a short alkyl σ bridge. Features of the ^1H and ^{13}C NMR spectra of swallowtailed perylenediimides are interpreted as resulting from restricted rotation about the imide C-N bond; the ^{13}C NMR spectra and stereochemistry of these molecules are contrasted with the case of the related bis-(2,5-di-*tert*-butylphenyl)perylenetetracarboxylic diimide.

Introduction

Donor- σ -acceptor (D- σ -A) molecules contain an electron-donor group (D) and an electron-acceptor group (A), connected through a nonconjugated σ -bond bridge that prevents the direct overlap of D and A energy levels.^{1,2} Aviram and Ratner proposed in 1974 that an organized monolayer of D- σ -A's with appropriate orbital energy levels should exhibit unidirectional electrical conductivity, that is, rectification of electricity.³ Such molecular-sized rectifiers hold promise for the miniaturization of electronic circuits as engineering approaches the scale of nanotechnology.⁴

For a monolayer to rectify, its molecules must be aligned in register between two electrodes, M_D and M_A (Figure 1a). This enables the molecules to work together when electrons flow from electrode M_A (acting as cathode) to A, and exit from D to electrode M_D (acting as anode); the extra electron in A's LUMO then tunnels through the $-\sigma-$ bridge to the vacancy in D's HOMO to complete the forward-direction flow. Individual molecules would work at cross purposes if the D and A groups were out of register (as in Figure 1b), and no rectification would be expected. One method commonly used to align D- σ -A molecules is the Langmuir-Blodgett (LB) technique,⁵ which requires the molecules to have polar and nonpolar ends. The D- σ -A part constitutes the polar end, while an alkyl-chain (lipid) tail typically provides the nonpolar end (Figure 1c). Monolayers of such compounds, formed

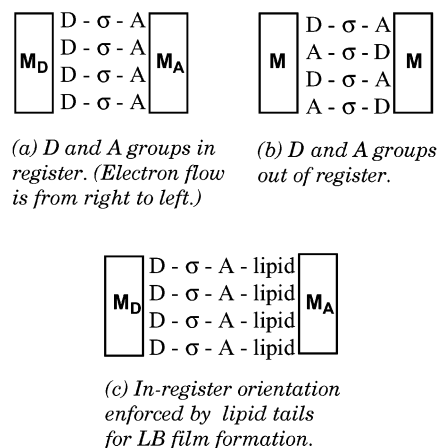


FIGURE 1. Alignment of D- σ -A molecules in monolayers.

spontaneously on an aqueous surface, can be lifted onto one electrode by careful dipping and withdrawal. Repeated treatment builds up multilayers. The second electrode is applied by evaporative metal techniques.^{3,4}

In the past, our group has used pyrene, trialkoxyphenyl, and ferrocene derivatives as donors, TCNQ and dinitrophenyl derivatives as acceptors, and carbamates as $-\sigma-$ bridges.⁶⁻⁹ Multilayers of one of our compounds with a pyrene donor and a dinitrophenyl acceptor gave hysteresis-free electrical rectification.¹⁰

Perylenebis(dicarboximide) as Acceptor. We have begun the preparation of a series of D- σ -A targets based

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(4) (a) Metzger, R. M. *Acc. Chem. Res.* **1999**, 32, 950-957. (b) Metzger, R. M. *Chem. Rev.* **2003**, 103, 3803-3834.

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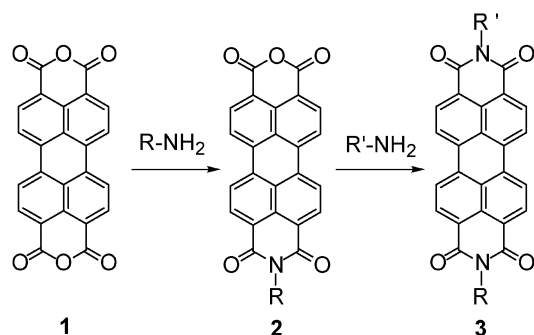
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on the good¹¹ acceptor perylene-4,5,9,10-bis(dicarboximide) (**3**), which can be prepared in principle from commercially available perylenetetracarboxylic dianhydride (**1**) by sequential imidizations.



In addition to being excellent acceptors, the perylenediimides have another striking advantage: the two synthetic handles of **1** can be exploited to produce the unsymmetrically disubstituted diimides (**3** with $R \neq R'$) needed for constructing D- σ -A-lipid systems. That is, one anhydride group of **1** can be used to connect the lipid tail needed for LB film formation (making monoimide **2**), and the other anhydride group can be used to attach the - σ - bridge and donor.

Swallowtail Solubilizers. Along with the advantages of perylenediimides, however, comes a major disadvantage. Their poor solubility (typically 1–2 mg/L) limits the amount of useful chemistry that can be accomplished with them.¹² Conventional **3**'s are not even capable of routine crystallizations. Langhals and co-workers have improved solubility by attaching 2° carbons in the middle of long chains.¹³ These create “swallowtail” diimides (like the 10-nonadecyl-disubstituted **3a**) which are amazingly soluble, to as much as 350 000 mg/L in heptane.¹⁴ Twin alkyl chains have similarly been used to improve the solubility of fluorene derivatives.¹⁵

A wide variety of unsymmetrical **3**'s with a single swallowtail have been reported,¹⁶ many coupled to various acceptor groups. Some of these groups can act as donors upon photoexcitation. Only one, however, with a pyrene donor and a C₁₃ swallowtail,^{16f} is a D- σ -A molecule of the type discussed above.¹⁷ We have chosen to use C₁₉ swallowtails, as that length gives the strongest solubilization, and the longer alkyl chains should help

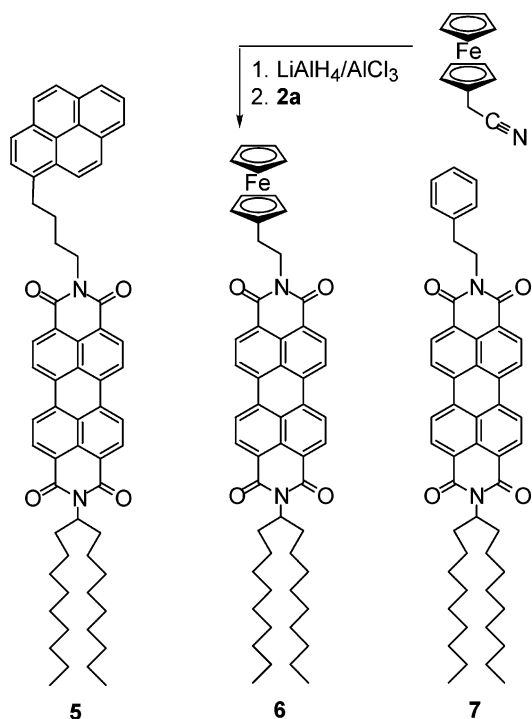
to encourage LB film formation. We report here the preparation of several of these D- σ -A-lipid targets.¹⁸ We also discuss some unusual features of the NMR spectra that stem from the swallowtails. The electrical characteristics of these targets will be reported separately.

Results and Discussion

Aryl and Ferrocenyl Donors. According to the literature, symmetrical **3**'s can be obtained by autoclaving an aqueous solution¹⁹ of the dianhydride **1** and a primary amine, or by heating them in molten imidazole with a Lewis acid catalyst.^{13,20} Subsequent semihydrolysis of the symmetric **3**'s can provide **2**'s.^{21,22} (This route is preferable to obtaining **2**'s by monoimidization of **1**, which proceeds poorly if the R groups are large.²¹) If a single swallowtail makes **2** adequately soluble, the conversion to unsymmetric **3** may be feasible by reflux in an aromatic solvent.

In practice, this procedure worked well in the formation of **4**, where R' contains a pyrene donor group. Treatment of **1** with the known 10-nonadecanamine (prepared by RedAl reduction of 10-nonadecanone oxime¹³) gave alkyl-swallowtailed **3a**, followed by semihydrolysis to **2a** and condensation of **2a** with commercial pyrenylmethylamine to give the target **4** (Scheme 1).

We also prepared, in a similar manner, a D- σ -A target with a four-carbon σ bridge to pyrene (**5**); this should allow us to see the effect of donor-acceptor



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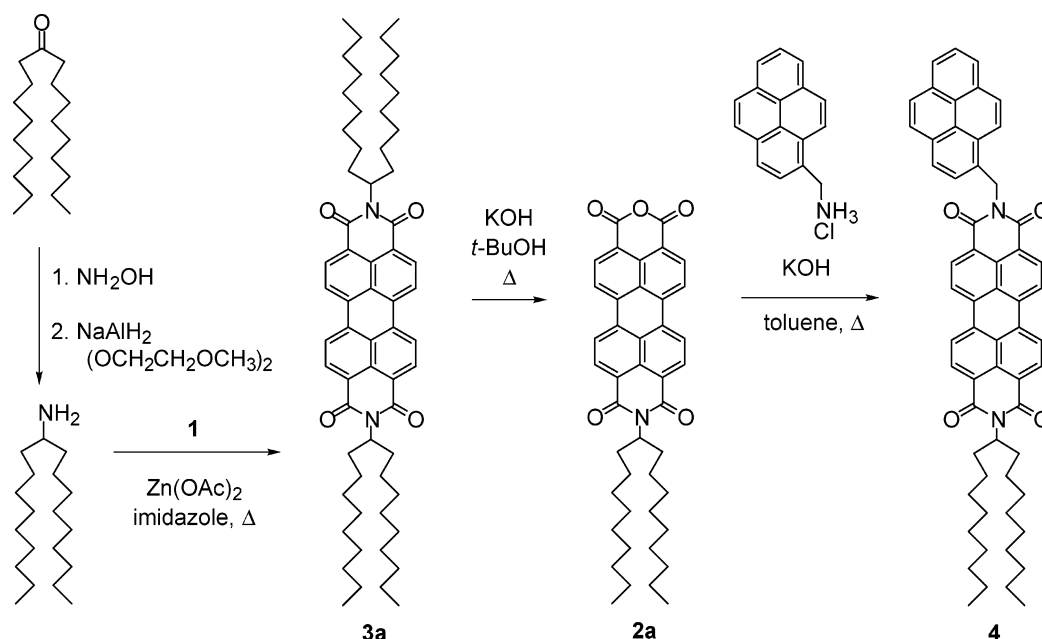
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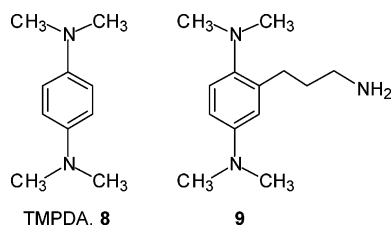
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SCHEME 1



separation on current flow. Such a long bridge could conceivably allow the donor and acceptor groups to fold back and interact intramolecularly, but we have successfully used 4- and 5-atom bridges previously.^{7,8,10} Compound **6** contains a ferrocene donor; the required ferrocenylethanamine precursor was prepared by LiAlH_4 reduction of ferrocenylacetonitrile.²³ Condensation of **2a** with phenethylamine gave **7**, which can serve as a control D- σ -A, since the phenyl group should not exhibit donor properties.

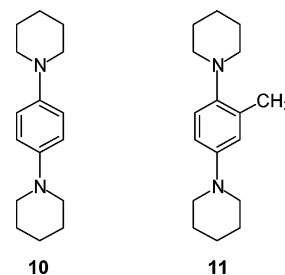
Tetramethylphenylenediamine Donor. We then turned to the excellent donor tetramethylphenylenediamine (TMPDA, **8**), whose nitrogen lone pairs release



electron density into the aromatic π system. Although TMPDA itself is readily available, it is more difficult to obtain derivatives. A handful of ring-alkylated TMPDA's have been reported,²⁴ but they lack suitable functional group handles.²⁵ We sought a TMPDA derivative such

as **9** that has a primary amine with which to attach the perylenediimide.

An alkyl group substituted on the TMPDA ring would be expected to diminish its donor properties somewhat by forcing the adjacent dimethylamino group out of planarity. For example, the reduction potential of the dipiperidinyl TMPDA analogue **10** is reported to be 192



mV vs NHE; the methylated derivative **11** has an $E_{1/2}$ of 351 mV.²⁶ This still represents a good donor, however, and even tetraethylphenylenediamines with two ring substituents have similar low reduction potentials.^{24f}

TMPDA has been directly alkylated by using radical reactions.²⁷ For example, photochemical activation of alkyl mercury compounds has been reported to give TMPDA alkylation, as shown in Scheme 2 for the formation of **12**.²⁸ We attempted a more straightforward generation of radicals,²⁹ by treating the *t*-BOC-protected bromoamine **14** (prepared from 3-bromopropylammonium bromide and *tert*-butyl dicarbonate³⁰) with tributyl tin hydride and AIBN. No reaction of **8** occurred with these

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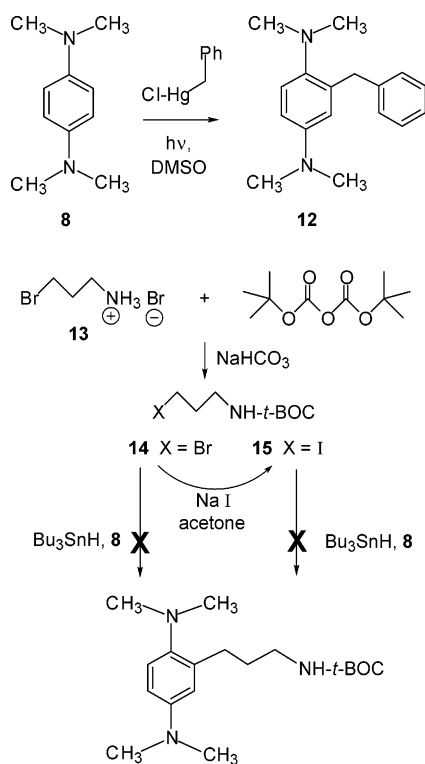
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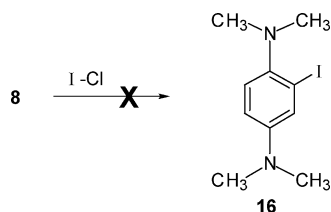
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SCHEME 2



reagents in refluxing benzene or toluene, so we converted **14** into the more reactive iodide **15** with sodium iodide in acetone and tried again. However, no reaction was apparent by TLC analysis.

We therefore turned to an indirect strategy, a palladium-catalyzed ring alkylation of iodinated TMPDA. Iodo-TMPDA (**16**) has been reported in the literature,^{24d}



where it was used in a $\text{Pd}(0)$ coupling to an aryl zinc species, but no information about its preparation or physical properties was given.

We first attempted to prepare **16** by direct iodination of TMPDA with I-Cl , following a literature procedure for 4-nitroaniline.³² In cold acetic acid, at least three products were apparent in TLC analysis; these were poorly separated by column chromatography, and no upfield signal diagnostic for iodinated aromatic carbon was apparent in the ^{13}C NMR spectrum. With 2 equiv of H_2SO_4 added to protonate the amino groups and moderate the process, no reaction was apparent, and in CCl_4 there was no reaction at room temperature and tar formation upon heating. In all cases, a blue-violet color formed, suggesting some oxidation by I-Cl of TMPDA to its radical cation, Wurster's blue.³³ Although substitu-

tion might proceed through such an intermediate,³⁴ we did not observe successful iodination.

We then followed a longer route as shown in Scheme 3, iodinating 4-nitroaniline with iodine and H_2O_2 as described by Toth³⁵ and reducing the nitro group of the resulting **17** with stannous chloride in hot concentrated HCl ^{36,37} to make **18**, followed by Giumanini and co-workers' procedure³⁸ for amino group permethylation with formaldehyde and sodium borohydride in acidic aqueous THF to give the desired iodo-TMPDA, **16**. This compound was found to be a liquid despite the presence of the iodine. The iodine is expected to force the adjacent dimethylamino group out of planarity with the benzene ring. This is consistent with aromatic NMR chemical shifts which are about 0.5 ppm downfield compared to simple predictions for **16**; with its resonance capabilities diminished, the nonplanar amino group apparently exerts a more electron-withdrawing shielding effect than it would if it were planar.

Heck reaction of **16** with acrylonitrile, palladium(II) acetate, triethylamine, and triphenylphosphine in a hot sealed tube gave a mixture of cis and trans alkenes **19**. The alkene mixture was saturated by catalytic hydrogenation with Pd/C in a Parr shaker to give the cyanoethyl compound **20**. Attempts to reduce the cyano group simultaneously with the double bond were not successful, but it was easily reduced in a separate step with LiAlH_4 in ether to give the desired **9**, which condensed easily with imide-anhydride **2a** in refluxing toluene to make the target compound **21**.

Di-Swallowtailed Perylenediimide Conformation. The proton NMR spectrum of **3a** showed two signals, well separated at 1.8 and 2.2 ppm, for the eight methylene hydrogens β to nitrogen in the swallowtail chains. The literature¹⁴ spectrum for **3a** reports only one signal at 2.1 ppm for these methylenes, although the literature^{21,22} spectrum for the imide-anhydride **2a** shows two signals for its corresponding four methylene hydrogens (in agreement with our findings for **2a**). We thought that a conformational restriction might be making the two methylenes of **3a** nonequivalent, but a sample warmed to 105 °C in pyridine- d_5 showed no changes in any swallowtail ^1H signals. Upon further consideration, we realized that the two hydrogens in each β methylene are in fact diastereotopic, which accounts for their distinct signals. One can think of these hydrogens as being in exo and endo positions in the MM2-minimized extended-chain conformation shown for **3a'**; the extended swallowtails are based on the crystal structure reported for **3** with C_{17} swallowtails.¹⁴ The corresponding β carbons are enantiotopic and give a single NMR signal at 32.0 ppm; this signal shows the expected HMQC correlation to both methylene H signals.

If **3a** were completely symmetrical, its four carbonyls would be identical. Instead, the ^{13}C NMR spectrum of **3a**

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SCHEME 3

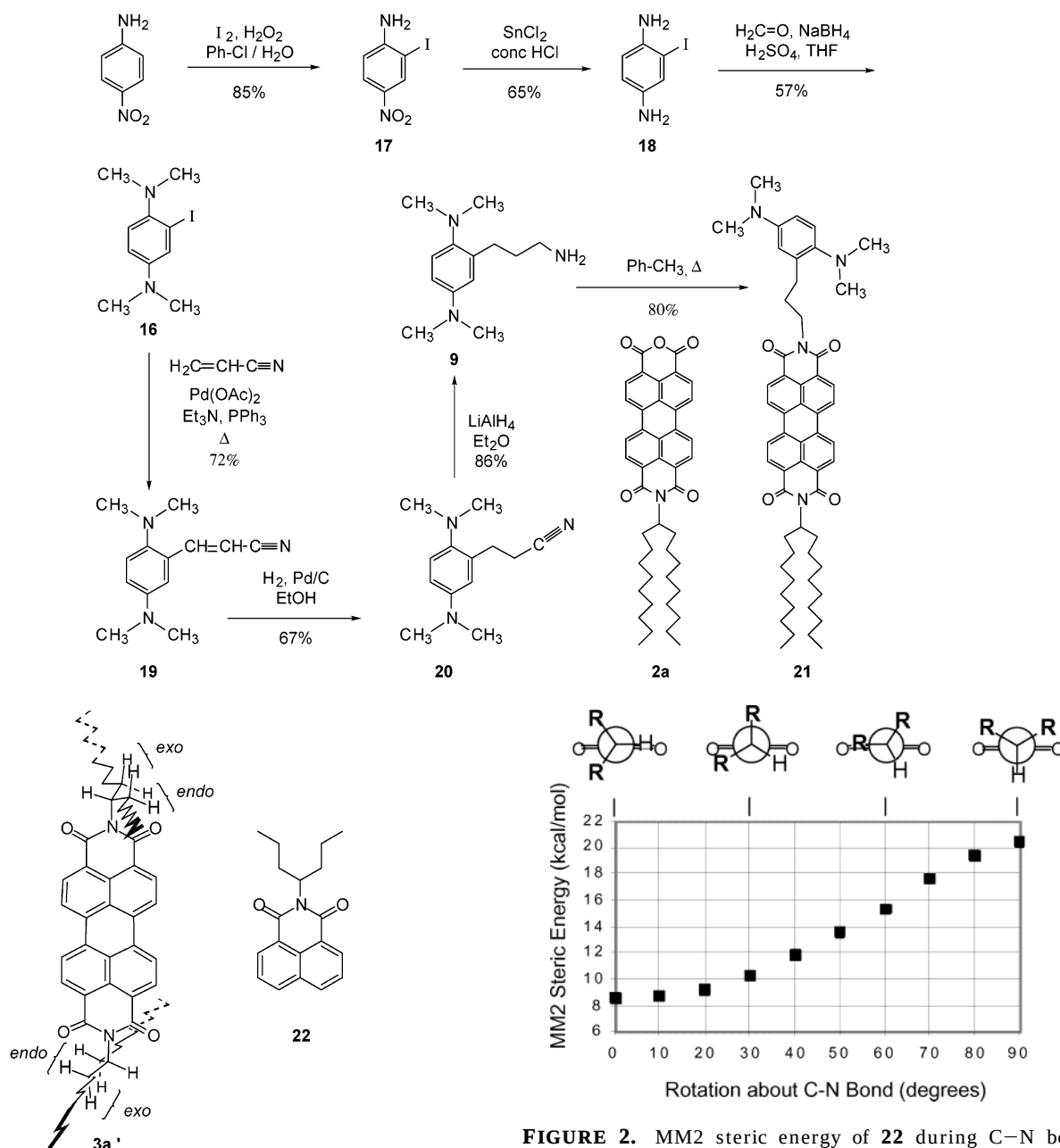


FIGURE 2. MM2 steric energy of **22** during C–N bond rotation.

showed two carbonyl signals (164.5 and 163.5 ppm), in agreement with the literature.¹⁴ Further, our ¹³C NMR spectrum of **2a** showed three carbonyls: one sharp (160.0 ppm) and two broad and weak (163.3 and 164.4 ppm). Literature reports^{21,22} for **2a** appear to have missed the weak signals, but this pattern is characteristic of our mono-swallowtailed products. The doubling of carbonyl signals from swallowtailed imides suggests that the swallowtails assume an asymmetrical conformation.

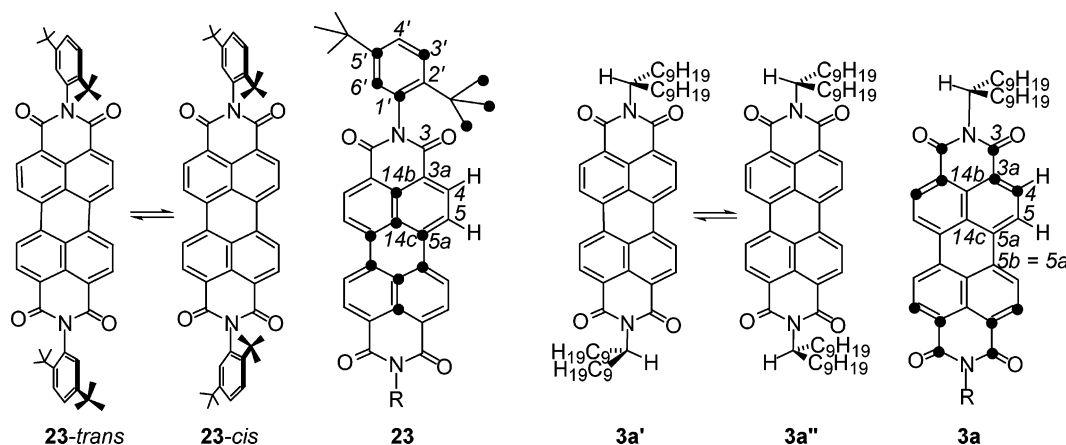
Langhals and co-workers³⁹ have studied the rotational barrier about the C–N bond of several swallowtailed **3**'s by line shape analysis of the carbonyl ¹³C NMR signals. Coalescence temperatures vary depending on the nature of the swallowtail; rotational barriers are about 15 kcal/

mol. To explore the conformational barrier, we performed MM2 calculations on **22** as a model for the swallowtail imide, starting with its swallowtail in the extended, all-anti conformation, and using a driver to rotate the C–N bond 360°. Lower energy conformations were found between 50° and 70° by introducing α,β gauche kinks in the swallowtail. Figure 2 shows the lowest energy found at each C–N rotation angle through 90° (further rotation gives equivalent conformations). The rotation barrier was 11.8 kcal/mol, in reasonable agreement with the experimental barrier. The asymmetry of the low-energy conformation (at 0° rotation) accounts for the distinct ¹³C signals: one carbonyl is eclipsed with the α hydrogen, while the other carbonyl is situated between the two swallowtail alkyls.

The doubling of carbon signals at low temperature and their exchange at higher temperature call to mind the

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SCHEME 4

**TABLE 1.** Aromatic and Carbonyl ^{13}C NMR Signals and Assignments for Swallowtailed Perylenediimides

av lit. ^a aromatic ^{13}C signals for 3 's (ppm)	lit. ^a assignment of ^{13}C signals from 3 's	^{13}C signals for 3a , rt (ppm)	^{13}C signals for 3a , 60 °C (ppm)	assignment of ^{13}C signals from 3a
164.0	3	164.5 (b ^b), 163.5 (b)	164.2 (b)	3
134.4	3a	134.3	134.7	5a
131.4	4	131.8 (b), 131.0 (b)	131.6 (b)	4
129.4	14b	129.5	129.9	14b
126.3	5a	126.3	126.7	14c
123.5	14c	124.0 (b), 123.2 (b)	123.9 (b)	3a
122.9	5	122.9	123.1	5

^a Reference 39. ^b These signals were broad and weak.

atropisomerism reported by Langhals and co-workers for bis(di-*tert*-butylphenyl)-substituted **23**.^{13,20} In that case, C–N bond rotation would result in interconversion of *cis* and *trans* isomers (Scheme 4). At room temperature, however, the system is too sterically hindered to rotate, and standard preparations make a stable mixture of the *cis* and *trans* diastereomers. In principle, the two isomers could give distinct NMR spectra. However, Langhals reported only tiny differences for two of the ^1H signals,²⁰ and reported single values for each of the mixture's ^{13}C positions.²¹ We took 125-MHz spectra of **23** and were able to distinguish 8 of the 17 carbon signals as distinct in the two isomers, giving doubled signals.

We were able to verify the literature peak assignments²¹ in the phenyl rings with the help of DEPT, HMQC, and HMBC spectra, except for two signals: HMBC coupling from the $\text{H}_{6'}$ singlet at 7.02 ppm to a CH peak at 126.6 ppm showed that it must be $\text{C}_{4'}$ rather than $\text{C}_{6'}$, and the return HMBC coupling from H_4 to doubled CH peaks at 127.8 ppm showed that they cannot be $\text{C}_{4'}$ but must be $\text{C}_{6'}$ instead.⁴⁰ Assignments in the perylene ring were made as discussed below for **3a**, a system which enables a final ambiguity to be resolved.

With assignments in hand, the doubled signals could be mapped onto the structure of **23**, as indicated by the dots in Scheme 4. In the phenyl groups, the more exterior parts (the $\text{C}_{5'}$ *tert*-butyl group and $\text{C}_{4'}$) were not affected. Interestingly, the interior *tert*-butyl carbon and its ring attachment $\text{C}_{2'}$ were also unaffected, even though the carbons surrounding them were doubled. In the perylene

skeleton, the three signals representing the eight interior carbons were doubled, which seems reasonable since they are between the interior *tert*-butyls whose relative positions change during isomerization. The average differences in chemical shifts for doubled carbons were 0.05 ppm for perylene skeleton carbons, 0.03 ppm for phenyl, and 0.01 ppm for *tert*-butyl. In contrast to **3a**, the four carbonyls in either isomer of **23** are equivalent, because the preferred conformation about each imide C–N bond is essentially perpendicular. The carbonyl signals for the two isomers of **23** were congruent.

In principle, an isomerization like **23**'s could account for signal doubling in swallowtailed **3a**, since C–N rotation interconverts diastereomers **3a'** and **3a''** (Scheme 4). However, such isomerism is not possible for single-swallowtailed imides such as **2a**, which also show carbonyl doubling. The doubling in swallowtailed imides is therefore best viewed as a local phenomenon caused by the asymmetric environment occurring near each swallowtail.

This asymmetry should extend beyond the carbonyl carbon, and in fact we see doubling of two other carbon signals in **3a** at room temperature. Langhals and co-workers also saw additional doublings at low temperature for **3**'s with short swallowtails.³⁹ The six aromatic ^{13}C signals of **3** were assigned by the Langhals group³⁹ as shown in Table 1; these are analogous to their assignments for **23**.²¹ We attempted to confirm those assignments in **3a**, but satisfactory HMBC spectra were unattainable at room temperature because the expected correlations from H_4 were absent. At 60 °C, however, the ^{13}C spectrum simplified, with the three sets of doubled peaks becoming broad singlets, and the 3-bond HMBC

(40) The numbering scheme used is the Chemical Abstracts numbering for **3**, anthra[2,1,9-*def*:6, 5, 10-*d'e'f'*]diisoquinoline-1,3,8,10-(2*H*,9*H*)-tetrone.

correlations from H₄ were revealed. HMBC correlation of the collapsed carbonyl to the downfield (δ 8.5) H identified it as H₄; HMQC correlations to H₄ and H₅ then identified C₄ and C₅. Only C_{5a} was 3-bond-coupled to both H₄ and H₅ (in the latter case, it was not the proximal C_{5a} but its adjacent twin C_{5b}, identical by symmetry, that was so coupled). C_{14b} was HMBC-coupled to H₄ only. The remaining two carbon signals, C_{14c} and C_{3a}, both showed HMBC coupling to H₅. However, C_{14c}, situated in the middle of the structure, should experience the same environment for both rotamers of **3a**, and therefore was distinguished as the signal that was not doubled at room temperature; this is the distinction that could not be made by looking only at **23**. By this analysis, three of the perylenediimide aromatic ¹³C signals have been misassigned in the literature (Table 1).

With structural assignments in hand, we concluded that the three doubled signals in **3a** represent the carbons that are closest to the restricted C–N bond; these are dotted in Scheme 4. Note that C_{14b}, also close to C–N, should nonetheless be undoubled because it has the same environment in the two rotamers. We discerned similar patterns of two doubled carbons in all swallowtailed derivatives except **4** and **5**, where apparent overlaps obscured expected peaks at 123.2 and 131.0 ppm, respectively. The long swallowtails of **3a** appear to significantly slow C–N rotation, since **3**'s with shorter swallowtails show doubling only at lower temperature.³⁹

Consistent with the problematic HMBC at room temperature was the unusual appearance of the aromatic protons: H₅ was a sharp doublet, but H₄ was quite broad. We attribute the H₄ broadening to the influence of the nearby C–N rotamers, whereas H₅, being more distant, escapes the effect. At 60 °C, H₄ becomes a sharp doublet. Similar spectra are obtained for other swallowtailed peryleneimides. For example, concentrated samples of **7** at 60 °C show four resolved, sharp doublets for the four aromatic pairs of perylene protons; however, at room temperature, the low-field signal broadens into an unresolved lump.

Conclusion

Five new D– σ –A targets were prepared with use of perylenetetracarboxylic diimide as the acceptor. The 10-nonadecyl swallowtail attached to one of the imide nitrogens imparted ample solubility to make all of the products amenable to chromatographic purification, while providing a lipid tail needed to promote LB film formation. Donor groups attached to the second imide nitrogen included a novel TMPDA derivative that was prepared with a 1° amine synthetic handle. Published NMR data for **2a**, **3a**, and **23** were revisited, and the effects of restricted bond rotation on the spectra were clarified. Film formation and electrochemical studies of these products will be reported elsewhere.

Experimental Section

N,N'-Di(10-nonadecyl)perylene-3,4,9,10-bis(dicarboximide) (3a).¹⁴ A mixture of 606 mg (1.55 mmol) of 3,4,9,10-perylenetetracarboxylic dianhydride (**1**), 1.07 g (3.78 mmol) of 10-nonadecanamine, 3.0 g of imidazole, and 214 mg (1.16 mmol) of zinc acetate was heated, with stirring, at 160 °C for 2 h. The mixture was then cooled, dissolved in CHCl₃, and

directly purified by column chromatography on silica gel (CHCl₃) to give 930 mg (66% yield) of a deep red solid (mp 97–99 °C, lit.¹⁴ mp 97 °C). ¹H NMR (CDCl₃) δ 0.79 (t, 12H), 1.21 (m, 56 H), 1.84 (m, 4H), 2.23 (m, 4H), 5.16 (m, 2H), 8.51 (d, 4H), 8.59 (br d, 4H). ¹³C NMR (CDCl₃, 77.16) δ 14.2, 22.8, 27.1, 29.4, 29.67, 29.68, 32.0, 32.5, 55.1, 122.9, 123.2, 124.0, 126.3, 129.5, 131.0, 131.8, 134.3, 163.5, 164.5. IR (PFE/PE cards) 2920 (m), 2852 (m), 1694 (m) cm⁻¹.

N-(10-Nonadecyl)-3,4,9,10-perylenetetracarboxylic Acid 3,4-Anhydride-9,10-imide (2a).^{21,22} A mixture of 0.24 g (0.26 mmol) of **3a**, 60 mg (0.90 mmol) of 85% KOH pellets, and 13 mL of *t*-BuOH was brought to reflux. After 30 min, an additional 2 pellets of KOH was added and heating was continued for an additional hour. The mixture was poured, with stirring, into a mixture of 13 mL of AcOH and 7 mL of 2 N HCl. The resulting red-brown precipitate was concentrated by centrifugation, washed twice with water, and dried at 80 °C. Chromatography on silica gel (90% CHCl₃/10% AcOH) yielded 94 mg (53% yield) of **2a**. ¹H NMR (CDCl₃) δ 0.80 (t, 6H), 1.20 (m, 28H), 1.85 (m, 2H), 2.21 (m, 2H), 5.15 (m, 1H), 8.55 (m, 6H), 8.65 (br, 2H). ¹³C NMR (CDCl₃) δ 14.2, 22.8, 27.1, 29.4, 29.7, 32.0, 32.4, 55.0, 118.9, 123.2, 124.0, 124.8, 126.4, 126.7, 129.5, 131.3, 131.8, 132.0, 133.6, 136.3, 160.0, 163.3, 164.4. IR (PE card) 1775 (s), 1732 (m), 1703 (m), 1661 (m) cm⁻¹.

N-(10-Nonadecyl)-N'-(1-pyrenylmethyl)perylene-3,4,9,10-bis(dicarboximide) (4). To 0.10 g (0.37 mmol) of 1-pyrenemethylamine hydrochloride in 10 mL of MeOH was added, with stirring, 3 pellets of 85% KOH. An equal volume of water was added and the cloudy mixture was extracted with methylene chloride, dried over MgSO₄, and concentrated by rotary evaporation. The resulting free base was dissolved in 10 mL of toluene containing 85 mg (0.13 mmol) of **2a**. The mixture was brought to reflux, held for 85 min, and then allowed to stand at room temperature overnight. The resulting precipitate was filtered and purified by chromatography on silica gel (90% CHCl₃/10% AcOH) to yield 130 mg of crude product. This material was rechromatographed and then crystallized from chloroform/hexanes to yield 30 mg (27%) of red solid, mp 275–290 °C. ¹H NMR (CDCl₃) δ 0.80 (t, 6H), 1.20 (m, 28H), 1.84 (m, 2H), 2.23 (m, 2H), 5.17 (m, 1H), 6.07 (s, 2H), 7.88 (m, 3H), 8.04 (m, 5H), 8.42 (m, 4H), 8.58 (m, 5H). ¹³C NMR (CDCl₃) δ 14.2, 22.8, 27.2, 29.4, 29.7, 32.0, 32.5, 41.6, 55.0, 123.0, 123.2, 124.1, 124.7, 124.8, 124.9, 125.2, 125.3, 126.0, 126.1, 126.3, 126.4, 127.3, 127.4, 127.9, 128.9, 129.4, 129.5, 130.2, 130.75, 130.82, 131.1, 131.3, 131.8, 131.9, 134.2, 134.8, 163.4 (w), 163.8, 164.7 (w). IR (PE card) 1694 (s), 1658 (s), 1651 (s), 1594 (s) cm⁻¹. Anal. Calcd for C₆₀H₅₈N₂O₄·H₂O: C, 81.04; H, 6.80; N, 3.15. Found: C, 81.22; H, 6.56; N, 3.20.

General Procedure for Formation of Mixed Diimides.

A mixture of **2a** with a 2- to 4-fold molar excess of the appropriate amine was refluxed in toluene for 1 h. The reaction mixture was then cooled, washed with 5% HCl followed by 10% K₂CO₃, dried over MgSO₄, and concentrated by rotary evaporation. Crude products were purified by chromatography on silica gel with CHCl₃ as the eluent to give red solids. Melting points were difficult to obtain due to the deep color of the materials and, in some cases, to apparent liquid crystalline behavior. The values given are where phase changes were first observed.

N-(10-Nonadecyl)-N'-(4-[1-pyrenyl]butyl)perylene-3,4,9,10-bis(dicarboximide) (5). **5** was prepared from pyrenebutylamine (Toronto Research Chemicals) in 52% yield; mp 255–258 °C. ¹H NMR (CDCl₃) δ 0.81 (t, 6H), 1.19 (m, 28H), 1.84 (m, 2H), 1.99 (m, 4H), 2.26 (m, 2H), 3.31 (m, 2H), 4.23 (m, 2H), 5.18 (m, 1H), 7.9 (m, 8H), 8.14 (d, 1H), 8.45 (m, 6H), 8.63 (br, 2H). ¹³C NMR (CDCl₃) δ 14.2, 22.8, 27.2, 28.2, 29.2, 29.4, 29.73, 29.76, 32.0, 32.5, 33.5, 40.3, 54.9, 122.2, 122.3, 122.4, 122.8, 123.0, 123.6, 124.36, 124.44, 124.47, 124.50, 124.7, 125.3, 126.1, 126.9, 127.2, 127.3, 127.99, 128.04, 128.4, 129.0, 129.4, 129.9, 130.4, 130.6, 130.9, 131.4, 133.6, 133.7, 136.2, 163.1, 163.6 (w), 164.6 (w). IR (PE card) 1691 (s), 1658 (s),

1650 (s), 1596 (m) cm^{-1} . Anal. Calcd for $\text{C}_{63}\text{H}_{64}\text{N}_2\text{O}_4$: C, 82.86; H, 7.06; N, 3.07. Found: C, 82.50; H, 7.21; N, 3.02.

***N*-(10-Nonadecyl)-*N'*-(2-ferrocenylethyl)perylene-3,4,9,10-bis(dicarboximide) (6).** The intermediate 2-ferrocenylethylamine was prepared as reported by Godillot et al.²³ A mixture of 85 mg of LiAlH_4 in 5 mL of anhydrous Et_2O was combined with a solution of 296 mg of anhydrous AlCl_3 in 7.5 mL of Et_2O . To this was added, with stirring, a slurry of 500 mg of ferroceneacetonitrile in 5 mL of Et_2O . After 1 h a small amount of water was carefully added, followed by 7 mL of 6 N sulfuric acid and 5 mL of water. The ether layer was separated and the aqueous layer was extracted with Et_2O , basified with KOH pellets, diluted with 30 mL of water, and reextracted. The resulting ether layer was dried over MgSO_4 and concentrated by rotary evaporation to give 146 mg (29% yield) of amine, which was used without further purification. ^1H NMR (CDCl_3) δ 1.40 (br s, 2H), 2.44 (t, 2H), 2.76 (t, 2H), 4.04 (m, 9H).

The diimide was prepared from 2-ferrocenylethylamine in 79% yield. The analytical sample was further purified by recrystallization from toluene and washing with hexanes; mp 214–216 °C. ^1H NMR (CDCl_3) δ 0.80 (t, 6H), 1.18 (m, 28H), 1.86 (m, 2H), 2.22 (m, 2H), 2.74 (m, 2H), 4.10 (s, 2H), 4.20 (s, 7H), 4.36 (m, 2H), 5.15 (m, 1H), 8.55 (m, 8H). ^{13}C NMR (CDCl_3) δ 14.2, 22.8, 27.2, 27.9, 29.4, 29.7, 32.0, 32.5, 41.3, 55.0, 67.6, 68.3, 68.8, 79.3, 85.2, 123.0, 123.1, 123.5, 124.2, 126.2, 126.4, 126.8, 129.3, 129.5, 131.1, 131.3, 131.9, 134.2, 134.6, 163.2, 163.6 (w), 164.6 (w). IR (PE card) 1695 (s), 1658 (s), 1650 (s), 1596 (m) cm^{-1} . Anal. Calcd for $\text{C}_{55}\text{H}_{60}\text{N}_2\text{O}_4\text{Fe}$: C, 76.02; H, 6.96; N, 3.22. Found: C, 76.06; H, 7.20; N, 3.05.

***N*-(10-Nonadecyl)-*N'*-(2-phenylethyl)perylene-3,4,9,10-bis(dicarboximide) (7).** **7** was prepared from phenethylamine in 72% yield, mp 225–228 °C. ^1H NMR (CDCl_3) δ 0.80 (t, 6H), 1.18 (m, 28H), 1.87 (m, 2H), 2.23 (m, 2H), 3.02 (m, 2H), 4.34 (m, 2H), 5.15 (m, 1H), 7.29 (m, 5H), 8.20 (d, 2H), 8.28 (d, 2H), 8.35 (d, 2H), 8.48 (br, 2H). ^{13}C NMR (CDCl_3) δ 14.2, 22.8, 27.2, 29.4, 29.7, 32.0, 32.5, 34.3, 42.0, 55.0, 122.96, 123.05, 123.4, 124.1, 125.9, 126.2, 126.3, 126.7, 128.7, 129.2, 129.3, 129.5, 131.0, 131.3, 131.8, 132.3, 134.2, 134.6, 138.8, 163.2, 163.5 (w), 164.6 (w). IR (PE card) 1698 (s), 1651 (s), 1594 (m) cm^{-1} . Anal. Calcd for $\text{C}_{51}\text{H}_{56}\text{N}_2\text{O}_4$: C, 80.49; H, 7.42; N, 3.68. Found: C, 80.20; H, 7.12; N, 3.53.

***tert*-Butyl (3-Bromopropyl)carbamate (14).** To a suspension of 3-bromopropylammonium bromide (**13**, 1.00 g, 4.57 mmol) in 20 mL of CHCl_3 was added NaHCO_3 (390 mg, 4.64 mmol) in 15 mL of water, di-*tert*-butyl dicarbonate (1.00 g, 4.58 mmol) in CHCl_3 , and KBr (1.10 g, 9.24 mmol). The mixture was refluxed for 18 h and then cooled. The layers were separated and the aqueous layer was extracted twice with CHCl_3 . The combined organic layers were dried over MgSO_4 and concentrated by rotary evaporation to yield 1.06 g of **14** (96%). ^1H NMR (CDCl_3) δ 1.41 (s, 9 H), 2.02 (m, 2 H), 3.23 (m, 2 H), 3.41 (t, 2 H), 4.65 (br s, 1 H), in agreement with the literature⁴¹ spectrum.

***tert*-Butyl (3-Iodopropyl)carbamate (15).** A solution of 560 mg (2.35 mmol) of **14** and 400 mg (2.67 mmol) of NaI in acetone was stirred for 16 h at room temperature. The mixture was then filtered and the filtrate was concentrated by rotary evaporation. The residue was dissolved in CHCl_3 , washed with $\text{Na}_2\text{S}_2\text{O}_5$, dried over MgSO_4 , and concentrated by rotary evaporation to yield 230 mg of **15** (34%). ^1H NMR (CDCl_3) δ 1.41 (s, 9 H), 1.97 (m, 2 H), 3.16 (m, 4 H), 4.62 (br s, 1 H), in agreement with the literature⁴² spectrum.

2-Iodo-4-nitroaniline (17). A mixture of iodine (8.09 g, 31.9 mmol), *p*-nitroaniline (8.08 g, 58.5 mmol), chlorobenzene (6 mL), and water (25 mL) was heated to 90 °C. Hydrogen peroxide (3% aq, 77 g) was added dropwise over a 15-min period. The mixture was heated to reflux for 25 h, and then was cooled, basified with NaOH pellets, and extracted with

CHCl_3 . The organic layer was dried over MgSO_4 and concentrated by rotary evaporation. The residue was crystallized from CHCl_3 to give 13.3 g (85%), mp 110–112 °C (lit.³⁵ mp 115 °C, 105 °C). ^1H NMR (CDCl_3) δ 4.90 (br s, 2 H), 6.67 (d, J = 15 Hz, 1 H), 8.02 (d $\times$ d, J = 15 Hz, J = 4 Hz, 1 H), 8.52 (d, J = 4 Hz, 1 H).

2-Iodo-1,4-benzenediamine (18). A slurry of **17** (5.27 g, 20.0 mmol) in 27 mL of conc HCl was warmed in a hot water bath. To this slurry was added, over 9 min and with stirring, a solution of 15.8 g (83.3 mmol) of SnCl_2 in 27 mL of conc HCl. After the solid dissolved and the yellow color diminished, the reaction was allowed to cool for 15 min then was placed on ice. NaOH (50% aq) was added until the mixture was strongly basic. The resulting thick mixture was cooled to 5 °C and filtered. The filtrate was crystallized from water to give 3.03 g (65%), mp 115–116 °C (lit.³⁶ mp 110–111 °C). ^1H NMR (CDCl_3) δ 3.30 (br s, 2 H), 3.68 (br s, 2 H), 6.57 (m, 2 H), 7.04 (d, J = 4 Hz, 1 H). ^{13}C NMR ($\text{DMSO}-d_6$) δ 85.3, 116.0, 116.5, 123.6, 139.0, 141.1.

2-Iodo-*N,N,N',N'*-tetramethyl-1,4-benzenediamine (16). A slurry of **18** (1.00 g, 4.27 mmol) and NaBH_4 (2.28 g, 60.2 mmol) in 35 mL of THF was added dropwise to a stirred solution of 7 mL of 3 M H_2SO_4 and 5 mL of 37% formalin in 35 mL of THF. The pH rose during the addition, and more sulfuric acid was added periodically to maintain the pH near 1–2. After 2 h, an additional 5 mL of formalin was added and the reaction was allowed to continue stirring overnight. Solid KOH was then added to raise the pH above 10. The organic layer was separated and the aqueous layer extracted twice with ether. The combined organic layers were dried over MgSO_4 and concentrated by rotary evaporation to yield an oil, which was purified by column chromatography (CHCl_3) to yield a light yellow oil, 710 mg (57%). ^1H NMR (CDCl_3) δ 2.66 (s, 6 H), 2.87 (s, 6 H), 6.70 (d $\times$ d, J = 14 Hz, J = 5 Hz, 1 H), 7.00 (d, J = 15 Hz, 1 H), 7.20 (d, J = 5 Hz, 1 H). ^{13}C NMR (CDCl_3) δ 41.0, 45.8, 99.9, 113.7, 120.7, 123.7, 144.8, 148.5. Anal. Calcd for $\text{C}_{10}\text{H}_{15}\text{N}_2\text{I}$: C, 41.40; H, 5.21; N, 9.65. Found: C, 41.10; H, 5.43; N, 9.29.

2-(2-Cyanoethenyl)-*N,N,N',N'*-tetramethyl-1,4-benzenediamine (19). Into a thick-walled Pyrex tube were placed 1.13 g of **16** (3.90 mmol), acrylonitrile (3.28 g, 61.9 mmol), Et_3N (0.59 g, 5.8 mmol), $\text{Pd}(\text{OAc})_2$ (40 mg, 0.16 mmol), and PPh_3 (0.32 g, 1.3 mmol). The tube was closed with a Teflon plug and placed in a steam bath overnight. After cooling, water was added to the mixture, and it was extracted three times with ether. The organic layers were washed with saturated brine, dried over MgSO_4 , and concentrated by rotary evaporation. The crude product was purified by column chromatography (CHCl_3) to yield a yellow-orange oil, 600 mg (72%), which NMR analysis indicated to be a 2:1 mixture of *E:Z* diastereomers. ^1H NMR (CDCl_3) δ 2.62 (s, 6 H), 2.90 (s, 3 H), 2.93 (s, 3 H), 5.39 (d, J = 20 Hz, 0.3 H), 5.88 (d, J = 28 Hz, 0.7 H), 6.71 (d, J = 5 Hz, 0.7 H), 6.82 (m, 1 H), 7.03 (m, 1 H), 7.44 (d, J = 5 Hz, 0.3 H), 7.62 (d, J = 20 Hz, 0.3 H), 7.85 (d, J = 28 Hz, 0.7 H). ^{13}C NMR (CDCl_3) δ 41.3, 45.8, 95.3, 110.8, 117.1, 119.3, 119.8, 120.5, 128.5, 128.8, 147.5, 149.2. IR (PE card) 2214 (m) cm^{-1} .

2-(2-Cyanoethyl)-*N,N,N',N'*-tetramethyl-1,4-benzenediamine (20). Into a Parr hydrogenation flask were placed 600 mg of **19** (2.79 mmol), 50 mL of EtOH, and a catalytic amount of 10% Pd/C. After the mixture was shaken overnight under pressurized H_2 , the catalyst was filtered off and the EtOH was concentrated by rotary evaporation to yield 410 mg (67%) of a colorless oil, which was used without purification in the next step. ^1H NMR (CDCl_3) δ 2.57 (s, 6 H), 2.67 (t, 13 Hz, 2 H), 2.89 (s, 6 H), 2.98 (t, J = 13 Hz, 2 H), 6.56 (d, 5 Hz, 1 H), 6.62 (d $\times$ d, J = 14 Hz, J = 5 Hz, 1 H), 7.09 (d, J = 14 Hz, 1 H). ^{13}C NMR (CDCl_3) δ 18.5, 28.6, 41.1, 46.2, 112.6, 114.4, 120.2, 121.9, 134.9, 143.0, 148.0. IR (PE card) 2247 (w) cm^{-1} . The analytical sample was purified by successive column chromatographies, first with 100:4:1 CHCl_3 :EtOH: NH_3 (aq), then with 100:1 CHCl_3 : NH_3 (aq) (dried over MgSO_4), and finally with CH_2Cl_2 .

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Anal. Calcd for $C_{13}H_{19}N_3$: C, 71.85; H, 8.81; N, 19.34. Found: C, 71.62; H, 8.88; N, 19.27.

2-(3-Aminopropyl)-*N,N,N',N'*-tetramethyl-1,4-benzene-diamine (9). To a stirred suspension of $LiAlH_4$ (512 mg, 12.8 mmol) in 20 mL of anhydrous ether was added, over a 5-min period, 410 mg of **20** (1.89 mmol) in 10 mL of anhydrous ether. After an additional 15 min, 35 mL of 15% NaOH was added, and the mixture was extracted with ether. The organic layer was dried over $MgSO_4$ and concentrated by rotary evaporation to yield 360 mg (86%) of an oil that was used without purification in the next step. 1H NMR ($CDCl_3$) δ 1.52 (br s, 2 H), 1.75 (m, 2 H), 2.59 (s, 6 H), 2.68 (m, 4 H), 2.87 (s, 6 H), 6.57 (s + d, 2 H), 7.04 (d $\times$ d, J = 12 Hz, J = 3 Hz, 1 H). ^{13}C NMR ($CDCl_3$) δ 27.9, 35.2, 41.3, 41.7, 46.1, 111.5, 114.6, 120.7, 138.3, 143.4, 147.8.

***N*-(9-Nonadecyl)-*N'*-(3-[2-(*N'',N'',N''',N'''*-tetramethyl-1,4-benzenediaminyl)propyl])perylene-4,5,9,10-bis(dicarboximide) (21).** A solution of **2a** (300 mg, 0.457 mmol) and **9** (300 mg, 1.36 mmol) in 15 mL of toluene was refluxed for 4 h. The mixture was cooled, concentrated by rotary evaporation, and purified by column chromatography ($CHCl_3$, then 9:1 $CHCl_3$:EtOH) to give 320 mg (80%) of a deep red, waxy solid, mp 64–67 °C. 1H NMR ($CDCl_3$) δ 0.80 (t, J = 11 Hz, 6 H), 1.17 (m, 28 H), 1.84 (m, 2 H), 2.16 (m, 4 H), 2.58 (s, 6 H), 2.83 (s + m, 8 H), 4.29 (m, 2 H), 5.16 (m, 1 H), 6.52 (d $\times$ d, J = 15 Hz, J = 5 Hz, 1 H), 6.66 (d, 5 Hz, 1 H), 7.00 (d, 14 Hz, 1 H), 8.61 (m, 8 H). ^{13}C NMR ($CDCl_3$) δ 14.2, 22.8, 27.1, 28.7, 28.8, 29.4, 29.7, 31.1, 32.0, 32.5, 41.0, 41.3, 46.0, 54.9, 111.5, 114.4, 120.8, 123.1, 123.2, 123.3, 123.4, 124.1, 126.5, 126.6,

129.5, 129.7, 131.2, 131.5, 132.0, 134.5, 134.7, 137.6, 143.3, 147.6, 163.5, 163.7 (w), 164.8 (w). IR (PE card) 1696 (s), 1659 (s), 1596 (s) cm^{-1} . Anal. Calcd for $C_{56}H_{68}N_4O_4 \cdot 2H_2O$: C, 74.97; H, 8.09; N, 6.24. Found: C, 75.19; H, 8.18; N, 6.08.

***N,N'*-Bis-(2,5-di-*tert*-butylphenyl)perylene-3,4,9,10-bis(dicarboximide) (23).**^{20,21} The commercial material was a mixture of cis and trans isomers, containing residual quinoline. 1H NMR ($CDCl_3$) δ 1.29 (18H, s, $C_{2'}-t-Bu$), 1.32 (18H, s, $C_{5'}-t-Bu$), 7.02 (2H, s, H_6), 7.46 (2H, d, $H_{4'}$, J = 8.4 Hz), 7.59 (2H, d, $H_{3'}$, J = 8.5 Hz), 8.70 (4H, m, H_5), 8.76 (4H, m, H_4). ^{13}C NMR ($CDCl_3$) δ 31.37 ($C_{5'}-Me$); 31.88, 31.89 ($C_{2'}-Me$); 34.41 ($C_{5'}-t-Bu$); 35.69 ($C_{2'}-t-Bu$); 123.45 (CH, C_5); 123.83 (C_{3a}); 126.56 (CH, $C_{4'}$); 126.94, 126.98 (C_{14c}); 127.79, 127.82 (CH, C_6); 128.97, 128.99 (CH, C_3); 130.01, 130.06 (C_{14b}); 132.10 (CH, C_4); 132.67, 132.69 ($C_{1'}$); 135.16, 135.21 (C_{5a}); 143.88 ($C_{2'}$); 150.30, 150.34 (C_5); 164.58 (C=O).

MM2 calculations were performed with Chem3D Pro 4.0.

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Supporting Information Available: Procedure for the preparation of 10-nonadecanamine; IR data for new prepared compounds; 1H NMR and ^{13}C NMR spectra for **2a**; HMBC spectra for **3a** (aromatic region) and **23**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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