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Synthesis of Donor-σ-Perylenebisimide-Acceptor Molecules Having PEG Swallowtails and Sulfur Anchors

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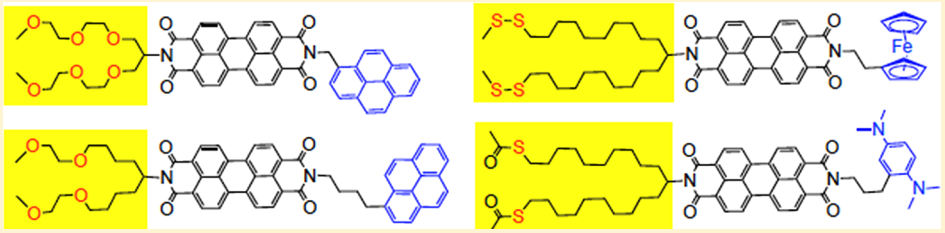
Supporting Information



ABSTRACT: Donor-σ-Acceptor (D-σ-A) molecules, arrayed in a monolayer between electrodes, can serve as molecular rectifiers. Using perylene-3,4,9,10-tetracarboxylic bisimide (PBI) as the acceptor allows the attachment of the donor group to one imide nitrogen and a solubilizing swallowtail, normally a long (e.g., C_{19}) alkane connected at midchain, on the other. Such an alkyl tail facilitates the formation of Langmuir−Blodgett (LB) monolayers. We have employed several modified swallowtails to make new D-σ-A molecules: poly(ethylene glycol) (PEG) swallowtails with 6 ether oxygens or with 4 ether oxygens to promote hydrophilicity in orienting LB monolayers, and alkyl swallowtails ending with sulfur anchors (thioacetate, thiol, or methyl disulfide) to stabilize attachment of the D-σ-A molecules to gold electrodes. The preparation and characterization of D-σ-A molecules containing combinations of these swallowtails with pyrene, ferrocene, and tetramethylphenylenediamine donor groups is described.

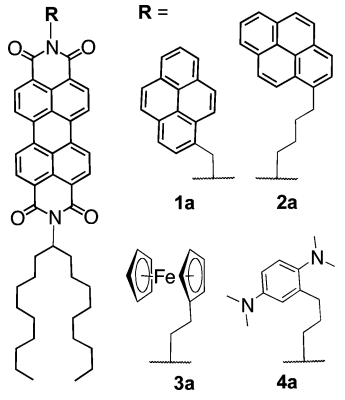
INTRODUCTION

Rectification (the unidirectional flow of current) through a Donor-σ-Acceptor (D-σ-A) molecule, where D is an electron-donating group, A is an electron-accepting group, and σ is a separating bridge of several bonds,[1−3] was first proposed by Aviram and Ratner in 1974.[4] Such organic molecular rectifiers have attracted attention as possible components of nanocircuits that could replace present-day silicon-based semiconductor devices.[5]

In the past quarter century, both experimental[6−8] and theoretical[9,10] studies have described rectifying behavior of D-σ-A molecules. To measure current through a potential D-σ-A rectifier, it is convenient to assemble a monolayer of the molecules and interrogate a collection of the monolayer molecules aligned in parallel. Monolayers may be formed by Langmuir−Blodgett (LB)[6,11−13] or self-assembled monolayer (SAM)[14−18] techniques. LB monolayers form when molecules organize themselves on the surface of an aqueous/air interface. To obtain a well-ordered LB monolayer, suitable for lifting onto a bottom electrode for electrical studies, an alkyl tail typically is attached to one end of the D-σ-A molecule to give it a hydrophobic end that will prefer to be in the air.[1] In contrast, formation of a SAM typically involves attaching a sulfur anchor to one end of the D-σ-A molecule, so that it will coordinate to the bottom Au electrode. The top electrode can be a scanning probe or can be created by evaporative metal techniques.[5]

We have previously described the synthesis (**1a**−**4a**, Chart 1)[1] and LB film formation and monolayer electrical properties

Chart 1. D-σ-A Molecules 1a−4a with a C_{19} Alkyl Swallowtail



(**1a**−**3a**)[6] of several D-σ-A molecules based on perylene-3,4,9,10-tetracarboxylic bisimide (PBI) as the acceptor. In order to provide adequate solubility and the required hydrophobic alkyl tail for LB film formation, a "swallowtail", a long alkyl chain connected at its center,[1,19] is attached to one imide end. (The letter **a** designates the C_{19} alkyl swallowtail shown; other letters will designate different swallowtail targets.) The other imide end holds the σ bridge to the donor group: pyrene (**1a**, **2a**), ferrocene (**3a**), or tetramethylphenylenediamine (**4a**). A

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well-packed LB film is not formed from **2a**, but LB monolayers of **1a** and **3a**, arranged between two electrodes in a "Au|D-σ-A|Au" sandwich, rectify electric current; **3a** has a rectification ratio between 14 and 28 at $\pm$1 V.[6]

In **1a**−**4a**, the donor end can be considered more polar than the C_{19} alkyl swallowtail end (even in the case of the donor pyrene, which is not particularly polar). It is therefore assumed that the donor end will prefer the aqueous subphase of the LB trough and will comprise the bottom of the monolayer, while the swallowtail end will be in air and comprise the top face (Figure 1a).[1] To have control of the direction of electron

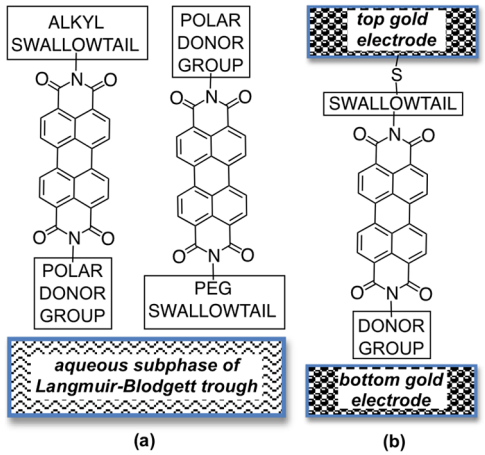


Figure 1. (a) Proposed orientation of swallowtailed D-σ-A molecules on an LB trough. (b) Stabilization with sulfur anchors of swallowtailed D-σ-A molecules in one of the two possible orientations.

transport across the monolayer, we wanted to be able to reverse the orientation of the LB film by changing the polarity of the swallowtail. Swallowtails with hydrophilic poly(ethylene glycol) (PEG) arms instead of alkyl arms would be more hydrophilic than the donors and might thereby reverse the film's orientation and its direction of rectification (Figure 1a). Fullerenes decorated with a PEG hemisphere[20a] and diblock copolymers with a PEG block[20b] can be oriented into Langmuir films in this way. In addition, PEG ether oxygens would provide a less-insulating layer compared to the hydrocarbon swallowtails, and this might allow for a greater tunneling current through the monolayer.

PEG tails are widely used to improve solubility,[21] and like alkyl swallowtails, various PEG tails have been used to improve the solubility of perylenebisimides.[22] PEG tails can impart liquid crystalline characteristics to PBI compounds,[23] which improve π−π stacking, allowing dynamic reorganization and easier processing. Cormier and Gregg[23] reported liquid-crystalline PBIs with branched propylimide-oligo(oxyethylene) or phenethylimide-oligo(oxyethylene) side chains, while Murray et al.[24] synthesized PBIs with short poly(ethylene oxide) tails. We planned to use a PEG swallowtail corresponding to the skeleton of the C_{19} alkyl swallowtail.

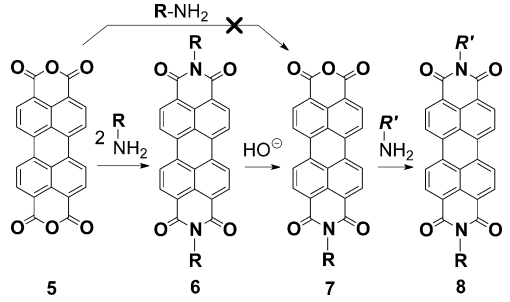
We are also interested in stabilizing the monolayers after their assembly into Au|D-σ-A|Au sandwiches. For example, the rectification ratios of **1a** and **3a** decrease on repeated voltage cycling, a phenomenon that is frequently seen in such systems.[5] A possible explanation for this attenuation is that molecules within the monolayer may flip their orientation in response to the cycling electric field. The incorporation of sulfur anchor groups at the ends of the swallowtail arms would inhibit the putative molecular flipping by coordinating the sulfur anchors to the gold electrode (Figure 1b). Thiol anchors have a strong, specific affinity toward gold[17,18] and form good SAMs, but the -SH group tends to be unstable, so thiols are often protected as thioesters (e.g., *S*-acetyl[25a]) or cyanoethyl thioethers[25b] and deprotected just before use. This strategy has been used to stabilize rectifying layers of a D-π-A molecule with an SAc anchor at the end of single alkyl tails of different lengths.[26a,b] *S*-Acetyl anchors themselves are capable of generating SAMs on gold, but the assembly process is slow and the properties of the resulting films differ from those of thiol-derived SAMs.[26c] High-quality SAMs can be formed from disulfides, but if these are unsymmetrical (e.g., RS-SCH$_3$), the coverage will differ from SAMs made from the corresponding thiols (RSH) or thioacetates (RSAc). Since SAMs to gold can be formed from all three of the above-mentioned sulfur groups, they are potential anchors for our D-σ-A molecules.

Here we report the synthesis of several D-σ-A molecules with PEG swallowtails, intended to reverse the orientation of the monolayers respective to the monolayers of molecules **1a**−**4a** and thereby reverse the direction of rectification, and D-σ-A molecules with sulfur anchors at the ends of alkyl swallowtails, to stabilize Au|D-σ-A|Au assemblies and sustain their rectification ratios, as well as making D-σ-A molecules capable of SAM formation. The formation and properties of monolayers made from these molecules and the investigation of their electrical properties will be described elsewhere.

RESULTS AND DISCUSSION

Unsymmetrical PBIs (**8**) are prepared from commercially available perylenetetracarboxylic bisanhydride **5** (Scheme 1). In

Scheme 1. General Procedure To Make Unsymmetrical PBIs 8



principle, one anhydride group of **5** could condense with a primary amine, R-NH$_2$, to make the monoimide monoanhydride **7**, followed by condensation of the other anhydride group with a second amine, R′-NH$_2$, to make **8**. In practice, the first condensation under typical conditions (e.g., molten imidazole and Zn(OAc)$_2$) usually affords only symmetrical bisimide **6**,[1,27,28] which is nicely soluble if R-NH$_2$ is a swallowtail. This bisimide is then semihydrolyzed to the imide anhydride **7** before introduction of the second amine,[1,29] which in our system adds the donor group. The preparation of appropriate swallowtail amines, R-NH$_2$, was therefore the first step in making the intermediates **7** required for the synthesis of the D-σ-A targets.

Swallowtail Amines (13). The PEG swallowtail amine **13b** (Scheme 2) was prepared by double Williamson alkylation of *N*,*N*-dibenzyl-protected serinol **10** with diethylene glycol monomethyl ether tosylate **11**, followed by hydrogenolysis of

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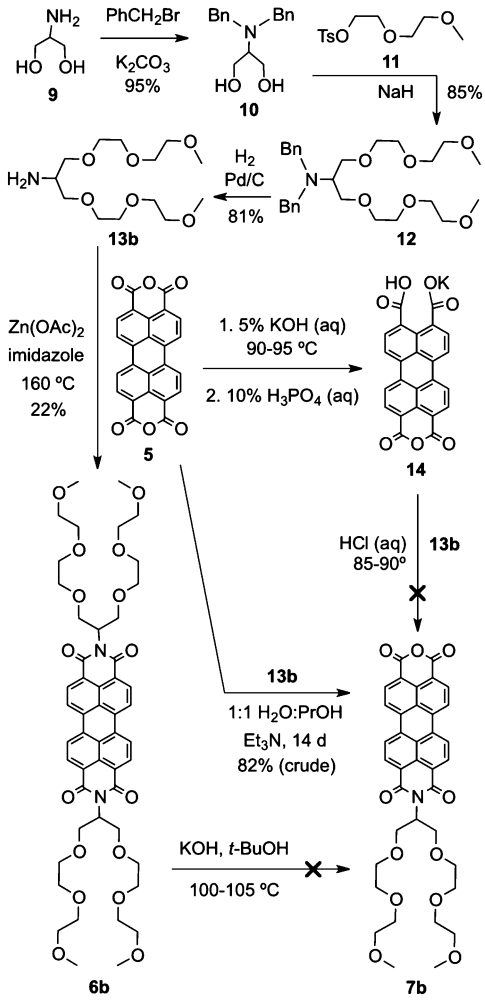
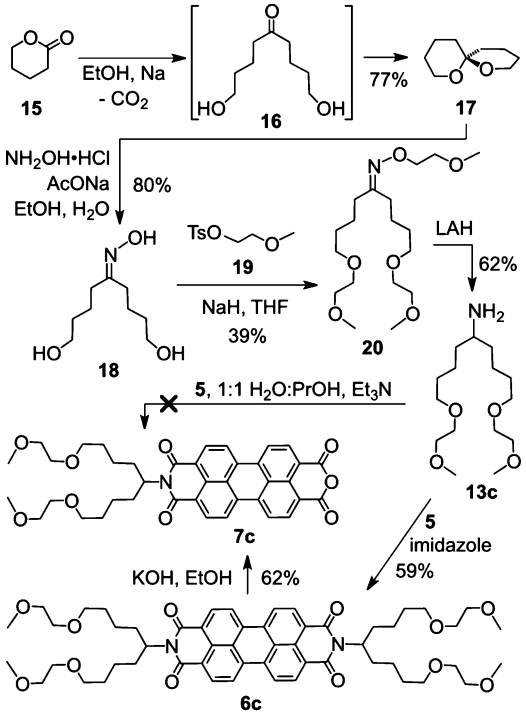
Scheme 2. Synthesis of PEG Swallowtail Imide Anhydride 7b



Scheme 3. Synthesis of Mixed-PEG Swallowtail Imide Anhydride 7c



the benzyl groups of the protected PEG amine **12**, as described previously.[21] We had converted **13b** to the symmetrical, water-soluble PBI **6b** as shown in Scheme 2; the water solubility of **6b** supported the idea that a single PEG swallowtail in a PBI would be hydrophilic enough to seek the water side of an LB monolayer. However, the troublesome solubility profile of the crucial imide anhydride **7b** prepared from **13b** (see below) prompted us to attempt an alternative, a "hybrid" swallowtail, **13c**, that ended in a PEG segment for hydrophilicity in an LB film but had alkyl character near to the imide nitrogen to promote better solubility in organic solvents (Scheme 3). We anticipated making amine **13c** from dihydroxyketone **16**, the product of a Claisen condensation of *δ*-valerolactone **15**. This condensation, however, is known to give only the spiroketal **17** (a pheromone of the female olive fly).[30] Ketal **17** is a thermodynamic sink for **16**, and various attempts to make **16** invariably produce **17** instead.[31−36] No reactions have been reported for **17**; this is attributed to its stable nature. We adopted Baker's procedure[30] for synthesizing **17** using a one-step Claisen condensation of **15**, and we then succeeded in converting **17** to its oxime **18** in good yield, essentially capturing **17** as it equilibrated with an open-chain form. Williamson alkylation of the hydroxyls of **18** with methoxyethyl tosylate **19** was accompanied by oxime alkylation, giving the triple-alkylated **20**. Alkylation of the oxime hydroxyl was not a concern, however, since $LiAlH_4$[37] in refluxing THF reduced the *N*-alkoxy group to the desired primary amine **13c**.

Our first attempt to obtain alkyl swallowtails with sulfur anchors was *via* transformation of terminal hydroxyl groups (Scheme 4). 11-Bromoundecanoic acid (**21**) was esterified and then underwent $TiCl_4$-catalyzed Claisen condensation[38] and decarboxylation to make the known dibromoketone **23**. Attempts to make the oxime of **23** were unsuccessful, presumably because of side reaction at the bromines, so the bromines were converted to hydroxyls by acetate substitution and methanolysis, yielding the dihydroxyketone **24**. In contrast to **17**, the intramolecular ketal is not favored in this larger system. Reductive amination of **24** gave the desired amine **13d**. This amine was converted to its imide anhydride **7d** *via* the bisimide **6d** before introduction of the thioacetate group (see below).

We also pursued an alternative route to obtain alkyl swallowtails with sulfur anchors that involved a swallowtail amine with terminal vinyl groups, **13h** (Scheme 5). 11-Undecenoic acid (**25**) underwent esterification, followed by Claisen condensation as before to give the divinyl ketone **27**[38] and then reductive amination to give **13h**. Again, introduction of the sulfur groups was delayed (see below) until after formation of the corresponding imide anhydride **7h**, prepared *via* the bisimide **6h**.

Perylenetetracarboxylic Monoimide Monoanhydrides (7). The general approach for making imide anhydrides outlined in Scheme 1 worked well for amines **13c**, **13d**, and **13h**. They condensed with bisanhydride **5** to make symmetrical bisimides **6c**, **6d**, and **6h**, followed by semihydrolysis[1,29,40] to the monoimide monoanhydrides **7c**, **7d**, and **7h**, as shown in Schemes 3, 4, and 5, respectively. In the case of **13d**, the standard conditions for making the bisimide were too harsh, but lowering the reaction temperature from 160° to 130° resulted in a satisfactory yield of **6d**.

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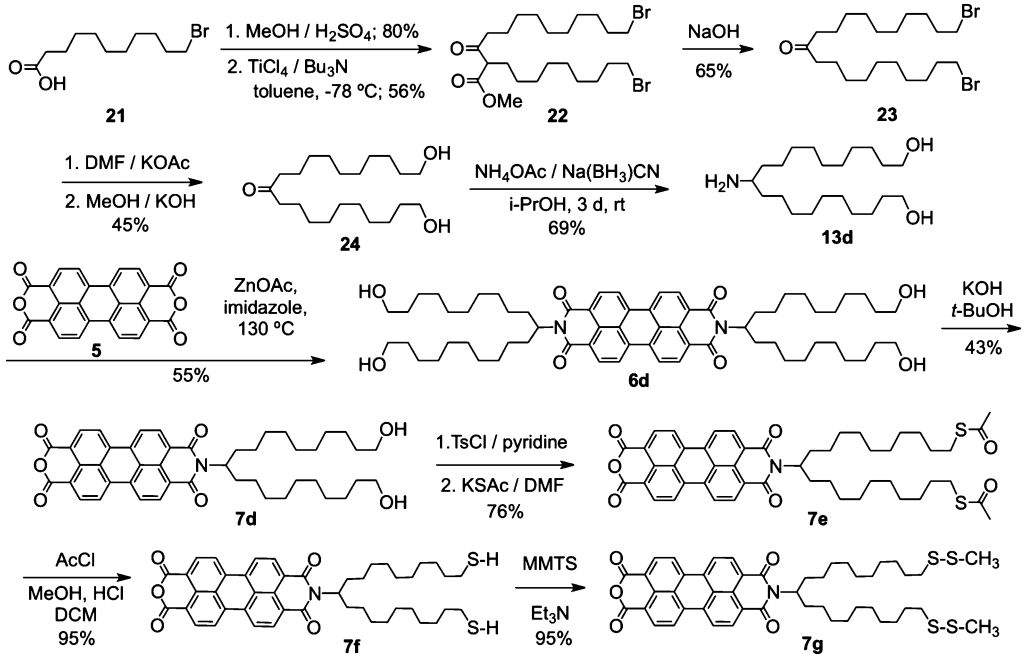
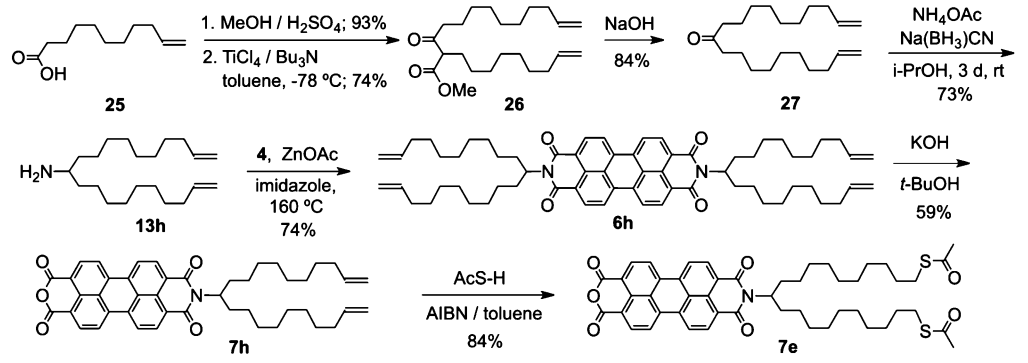
Scheme 4. Synthesis of Sulfur-Anchored, Alkyl-Swallowtailed Imide Anhydrides 7e, 7f, and 7g



Scheme 5. Alternate Synthesis of Thioacetate-Anchored, Alkyl-Swallowtailed Imide Anhydride 7e



The swallowtails of **6d** and **6h** closely resemble alkyl swallowtails, differing only in the presence of hydroxyl (**6d**) or vinyl (**6h**) groups at the distal ends of the swallowtail arms. A modification of the procedure was needed to prepare intermediate **7c** (Scheme 3), in which the swallowtail is PEG-like for the five distal skeletal atoms of each arm, but alkyl for the four skeletal atoms of each arm closest to the perylenebisimide. The standard semihydrolysis conditions of KOH in *t*-BuOH were unsuccessful with **6c**, because the reaction was too fast and both imides were hydrolyzed. A change of solvent to ethanol, however, gave a satisfactory yield (62%) of **7c**. As hoped for, monoimide monoanhydride **7c**, in contrast to PEG analogue **7b**, was soluble in organic solvents, and hence we could easily verify its structure using NMR.

Difficulties arose when we attempted to prepare the monoimide monoanhydride containing a full PEG swallowtail (**7b**) by the standard method. The PEG-amine **13b** converted easily to PBI **6b** (Scheme 2). However, in contrast to the alkyl-like monoimide monoanhydrides **7c**, **7d**, and **7h**, which had been soluble in organic solvents and therefore easily isolated following semihydrolysis, **7b** was insoluble in common organic solvents, complicating its purification. We were unable to isolate adequate amounts of **7b** by this method and therefore turned to alternate methods.

In our hands, Tröster's method[41] of making imide anhydrides directly from the monoanhydride monopotassium salt (**14**) of **5** was not successful with the PEG amine **13b** (Scheme 2). The crude reaction mixture failed to show anhydride carbonyl peaks in the infrared spectrum. (We also tried Tröster's salt **14** with the dihydroxyalkyl swallowtail amine **13d** but obtained an intractable polar product.) Pasaogullari and Demuth's modified procedure[42] employing Tröster's salt[41] also failed in preparing **7b**.

Nagao and Misono's method (lengthy refluxing of **5** with a primary amine in a H_2O/PrOH/Et_3N mixture[43]) was able to convert PEG amine **13b** into imide anhydride **7b** (Scheme 2). However, compound **7b** was not soluble in common organic solvents, although it was soluble in basic solvents such as morpholine, pyridine, and diethylamine. Due to its poor solubility, it was difficult to verify its purity following purification attempts by column chromatography; consistent with the thermal instability of PEGs,[44] sublimation was also unsuccessful. Crude **7b** was therefore used to carry the synthesis forward. The Nagao–Misono method is generally less useful for large alkyl swallowtails, presumably because of

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their poor solubility in the polar solvents, but we thought the half-PEG, water-soluble amine **13c** might be a worthy substrate. However, only trace amounts of monoimide monoanhydride **7c** were obtained with this method (Scheme 3).

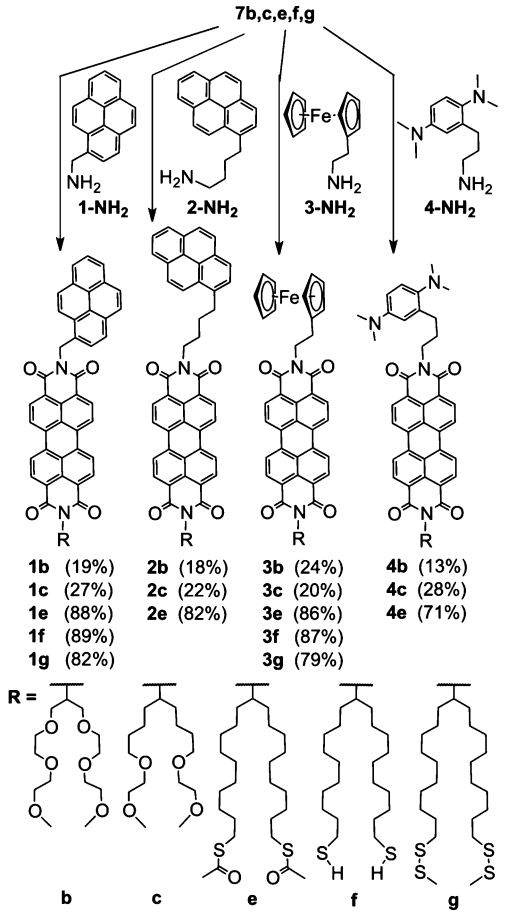
Introduction of Sulfur End Groups into Swallowtailed Monoimide Monoanhydrides. With the hydroxyl-tipped alkyl-swallowtailed imide anhydride **7d**, tosylation and displacement with thioacetate afforded the thioacetate-tipped **7e** (Scheme 4). This compound could also be obtained from the vinyl-tipped imide anhydride **7h** by a double radical-chain addition of thioacetic acid[45] to the terminal double bonds (Scheme 5), a reaction that required dry solvents and an inert atmosphere to obtain good yields. The route to thioacetyl-tipped **7e** was shorter *via* the divinyl swallowtail **13h** compared to the diol **13d**, and the overall yield from starting C_{11} acid was much better for the divinyl route (21%) compared to the diol route (2%).

The bisthioacetate imide anhydride **7e** was converted to the dithiol imide anhydride **7f** by treatment with acetyl chloride in MeOH,[46] which provided an acidic environment that promoted methanolysis (Scheme 4). In turn, the dithiol **7f** was converted to the bis(methyldisulfide) **7g** by treatment with methyl methanethiosulfonate.[47]

Conversion of Monoimide Monoanhydrides 7 to Unsymmetrical Bisimides. The condensation of perylene monoimide monoanhydrides **7** with donor amines pyrenylmethyl (**1-NH$_2$**), pyrenylbutyl (**2-NH$_2$**), ferrocenylethyl (**3-NH$_2$**), or TMPDA-propyl (**4-NH$_2$**) to make unsymmetrical bisimides was straightforward (Scheme 6). Target D-σ-A molecules **1b**, **2b**, **3b**, and **4b**, with the full PEG swallowtail, were made by refluxing crude PEG imide anhydride **7b** and the appropriate donor amine in pyridine overnight. In contrast to the precursor imide anhydride **7b**, all of these PBI targets were soluble in chloroform, and recrystallization ($CHCl_3$/hexane) followed by column chromatography (99:1 $CHCl_3$/MeOH) resulted in pure products. Target D-σ-A molecules **1c**, **2c**, **3c**, and **4c** with mixed alkyl-PEG swallowtails were made by refluxing crude imide anhydride **7c** with the appropriate donor amine in toluene. Target D-σ-A molecules **1e**, **2e**, **3e**, and **4e**, containing thioacetate-anchored alkyl swallowtails, were made by refluxing crude imide anhydride **7e** with the appropriate donor amine in toluene; in the case of the reaction of **4-NH$_2$**, slow addition of the amine was required to suppress side reaction of the thioacetates. We decided to utilize the other two, less widely used sulfur anchor groups, thiol **f** and disulfide **g**, with two of the donors, **1-NH$_2$** and **3-NH$_2$**. Condensation of imide anhydrides **7f** and **7g** with these amines gave targets **1f**, **1g**, **3f**, and **3g**.

Attempted Direct Condensation to Unsymmetrical Bisimides. Although the final condensations shown in Scheme 6 were straightforward, the yields were disappointing (around 20%) for the PEG and mixed-PEG swallowtails **b** and **c**, compared to the alkyl swallowtails **e**, **f**, and **g** (around 80%). We therefore attempted an alternative "direct" condensation by treating the bisanhydride **5** with PEG swallowtail amine **13b** combined with either **1-NH$_2$** or **3-NH$_2$**. Such attempts to avoid the isolation of the monoimide monoanhydride intermediate are usually not very successful:[32] even if both amines have similar reactivity, there will be two symmetrical bisimide products along with the desired crossed product, and these will be difficult to separate. However, if only one of the amines is a swallowtail, the separation problem may simplify since the swallowtail may impart unusual solubility to bisimides

Scheme 6. Formation of Unsymmetrical PBI D-σ-A Targets



containing it;[14] in this case, the direct procedure is much simpler and shorter than the conventional route of Scheme 1. In the event, treatment of **5** with 5- to 10-fold excesses of both donor amine and **13b** in either hot pyridine or imidazole for 1.5 d resulted in crude products from which no color was extractable into $CHCl_3$. Since the target PBIs are deep red and soluble, the procedure was unsuccessful.

Carbonyl ^{13}C Peaks. For PBIs with alkyl swallowtails (e.g., **1a**–**4a**), slow rotation about the N–CH bond, along with a preferred conformation that places the CH bond in the plane of the carbonyls, makes the two carbonyls nonequivalent on the NMR time scale. This gives rise to two weak carbonyl peaks in the ^{13}C NMR spectrum.[1] We observed similar nonequivalence in the symmetrical PBIs that had alkyl tails tipped with hydroxyl (**6d**) and vinyl (**6h**) groups and in imide anhydrides containing those swallowtails (**7d**, **7h**) or alkyl swallowtails tipped with sulfur-containing groups (**7e**, **7f**, **7g**). Changing to a PEG swallowtail apparently increases the rotation rate about the N–CH bond, since only one signal was observed for the swallowtail carbonyls in the bisimides **6b**[21] and **1b**–**4b**. In agreement, MM2 calculations of a model swallowtail with oxygens γ to the N predicted a rotation barrier of 8.5 kcal/mol, lower than the prediction for an alkyl swallowtail of 11.8 kcal/mol.[1] The hybrid alkyl-PEG swallowtail would be expected to be dominated by its alkyl portion, and the symmetrical bisimide **6c** indeed showed two carbonyl peaks. The results were not so clear-cut for the imide anhydride **7c** and the unsymmetrical bisimides **1c**–**4c**. One weak carbonyl peak could be one of a pair, with the second peak coincident with a larger carbonyl

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peak from the other end of the molecule. Interestingly, this same situation was observed in unsymmetrical bisimides with sulfur-tipped swallowtails (**1e**−**4e**, **1g**, **3g**), in which the nature of the swallowtail is clearly alkyl.

CONCLUSIONS

We report here the synthesis of 16 new D-σ-A molecules, combining the PBI acceptor with three different donor groups (with two different tether lengths for the pyrene donor) and five different swallowtails. We tried several approaches for constructing the required unsymmetrical perylene bisimide architecture, and it is interesting that the approaches gave such varied results. The Tröster salt and direct condensation approaches, useful in some systems, were completely unsuccessful here. The familiar semihydrolysis of PBIs **6** to imide anhydrides **7** shown in Scheme 1 was the preferred route for alkyl-like swallowtails, including the mixed alkyl-PEG **13c**. In contrast, the full PEG swallowtail amine **13b** was best managed with the basic equilibration method of Nagao and Misono.

EXPERIMENTAL SECTION

General Methods. Oxygen- and/or moisture-sensitive reactions were carried out under N_2 in glassware that was dried under vacuum and purged with N_2 prior to use. Reagents and solvents were purchased from commercial vendors and used as received. ^{1}H and ^{13}C NMR spectra were recorded on 300 or 500 MHz spectrometers at 25 °C. IR spectra were obtained with an FTIR spectrometer. Chromatography was performed using 60 Å silica gel.

2-(*N*,*N*-Dibenzylamino)-1,3-propanediol (10). 2-Aminopropane-1,3-diol (5.21 g, 57.2 mmol) and anhydr potassium carbonate (24.5 g, 177 mmol) were suspended in ethanol (200 mL). Benzyl bromide (30.3 g, 177 mmol) was added dropwise over 30 min with stirring. After the mixture had refluxed for 3 h, solids were separated by filtration, and volatiles were removed under reduced pressure. The residue was dissolved in EtOAc; the solution was washed with water, aq $NaHCO_3$, and brine and dried with anhyd $MgSO_4$; and the solvent was removed under reduced pressure. The crude mixture was purified by recrystallization from 1:1.2 benzene/hexane to give 14.7 g (95%) of white needles. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40−7.25 (m, 10 H), 3.74 (s, 4 H), 3.69 (m, 2 H), 3.59 (m, 2 H), 2.99 (m, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.2, 128.8, 128.3, 127.3, 59.8, 59.7, 53.9. NMR spectra are in agreement with the literature.[21,48]

2-(2-Methoxyethoxy) Ethyl Tosylate (11). To a solution of diethyleneglycol monomethyl ether (4.35 g, 36.2 mmol) in 15 mL of THF, cooled at 0 °C, was added NaOH (2.46 g, 61.5 mmol) dissolved in 15 mL of water with vigorous stirring. To this mixture was added dropwise a solution of tosyl chloride (8.28 g, 43.4 mmol) in 15 mL of THF over 10 min at 0 °C. The reaction mixture was then raised to rt and stirred for 1 h under N_2. It was then extracted twice with 50 mL of diethyl ether, and the organic layer was washed with 1 M aq NaOH and water and dried with anhyd $MgSO_4$. Solvent was removed under reduced pressure to yield 9.0 g (91%) of colorless liquid **11**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 6.0 Hz, 2H), 7.31 (d, J = 6.0 Hz, 2H), 4.17 (t, J = 6.0 Hz, 2H), 3.70 (t, J = 6.0 Hz, 2H), 3.58 (m, 2H), 3.47 (m, 2H), 3.34 (s, 3H), 2.42 (s, 3H). NMR spectrum is in agreement with the literature.[49]

***N*,*N*-Dibenzyl-2,5,8,12,15,18-hexaoxa-10-nonadecanamine (12).** THF (50.0 mL) was added to NaH (60% suspension in mineral oil) (0.80 g, 33.4 mmol), and the mixture was stirred to make a suspension. A solution of **10** (4.12 g, 15.1 mmol) in 15 mL of THF was then added dropwise under nitrogen, and after 30 min of stirring, a solution of **11** (9.16 g, 33.4 mmol) in 20 mL of THF was added dropwise. The reaction mixture was refluxed overnight, cooled, and treated carefully with MeOH to destroy excess NaH. The solvent was removed under reduced pressure and the resulting brown oil was extracted 4 times with 20 mL portions of hot ether. The combined ether fractions were concentrated by rotary evaporation to give 5.12 g (71%) of a yellowish liquid, R_f (EtOAc) 0.47. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (m, 4H), 7.28 (m, 4H), 7.20 (m, 2H), 3.78 (s, 4H), 3.55 (m, 20H), 3.37 (s, 6H), 3.10 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.8, 128.7, 128.1, 126.7, 72.0, 70.7, 70.6, 70.5, 70.4, 59.0, 56.2, 55.2. NMR spectra are in agreement with the literature.[21]

2,5,8,12,15,18-Hexaoxa-10-nonadecanamine (13b). The *N*,*N*-dibenzyl PEG-amine **12** (4.00 g, 8.41 mmol) was dissolved in 110 mL of MeOH, and 2.5 g of 10% Pd/C catalyst was added. The mixture was hydrogenated overnight in a Parr shaker at 55 psi of H_2. The reaction mixture was then filtered, and the solvent was removed under reduced pressure to give 2.0 g (81%) of an oil, R_f (72:18:10 CH_2Cl_2/NH_2OH(aq)/MeOH) 0.51. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60 (m, 12H), 3.51 (m, 6H), 3.35 (m, 8H), 3.17 (m, 1H), 2.04 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 72.0, 71.9, 70.6, 70.56, 70.51, 70.4, 59.1. IR (thin film) 3522, 3364, 3290, 2891 cm^{-1}. NMR and IR are in agreement with the literature.[21]

***N*,*N*′-Di[10-(2,5,8,12,15,18-hexaoxanonadecyl)]perylene-3,4,9,10-bis(dicarboximide) (6b).** PEG amine **13b** (212 mg, 0.71 mmol), dianhydride **5** (128 mg, 0.32 mmol), imidazole (2.62 g), and $Zn(OAc)_2$ (catalytic amount) were heated at 165 °C overnight. The reaction mixture solidified upon cooling and was dissolved in MeOH, then run through a Sephadex column to obtain 75 mg (22%) of deep-red waxy solid, R_f (2:1 MeOH/EtOAc) 0.70. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (m, 4H), 8.58 (m, 4H), 5.72 (m, 2H), 4.19 (m, 4H), 3.99 (m, 4H), 3.72 (m, 4H), 3.61 (m, 12H), 3.56 (m, 8H), 3.42 (m, 8H), 3.28 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 134.6, 131.7, 129.7, 126.4, 123.6, 123.2, 72.0, 70.63, 70.62, 70.5, 69.4, 59.1, 52.2. IR (KBr) 1700 (C═O), 1654 (C═O) cm^{-1}. NMR and IR are in agreement with the literature.[21]

***N*-[10-(2,5,8,12,15,18-Hexaoxanonadecyl)]-3,4,9,10-perylenetetracarboxylic Acid 3,4-Anhydride 9,10-Imide (7b).** To a mixture of perylenedianhydride **5** (498 mg, 1.27 mmol) and the PEG swallowtail amine **13b** (372 mg, 1.25 mmol) in 40 mL of propanol and water (1:1) was added triethylamine (1.68 g, 16.6 mmol), and the reaction was heated for 15 d at 120 °C. The reaction mixture was treated with excess 5% HCl at 120 °C for 10 min, cooled to room temperature, filtered, and dried to give 0.70 g (82%) of the perylene imide anhydride **7b** as a waxy solid. Due to limited solubility, crude material was carried further (see below), and no NMR data was collected. IR (KBr) 1768 (s) (anhydride C═O), 1733 (m) (anhydride C═O), 1693 (s) (imide C═O), 1648 (s) (imide C═O) cm^{-1}. HRMS (TOF MS ES$^+$) calcd for $C_{37}H_{35}NO_{11}$ 669.2108; found 669.2109.

1,7-Dioxaspiro[5.5]undecane (17). Sodium metal (1.15 g, 50.0 mmol) was dissolved in 50 mL of ethanol. To this was added dropwise a solution of δ-valerolactone (**15,** 10.0 g, 100 mmol) in 15 mL of ethanol at 0 °C, and then the mixture was refluxed for 5 h, cooled, acidified with 5% HCl, and refluxed again for 30 min. The reaction mixture was then co-distilled with water. The water distillate was extracted with ether, which was then dried over anhyd $MgSO_4$ and concentrated to give 6.00 g (77%) of clear colorless liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.69 (d × t, J = 7.1, 14.0 Hz, 2H), 3.63 (m, 2H), 1.83 (m, 2H), 1.5 (m, 10H), consistent with the literature[4] values. IR (liquid film) 1652 cm^{-1}.

1,9-Dihydroxy-5-nonanone Oxime (18). 1,7-Dioxaspiro[5.5]-undecane (**17**, 6.00 g, 38.4 mmol), hydroxylamine hydrochloride (2.77 g, 39.9 mmol), and sodium acetate (3.24 g, 39.5 mmol) were added to a mixture of 40 mL of ethanol and 30 mL of water, and the reaction mixture was heated with constant stirring and a closed condenser to prevent the escape of the volatile **17**. This reaction was conducted at 40 °C for 6 h, 60 °C for 4 h, and then at 80 °C for 26 h. The reaction mixture was cooled to rt, basified with aq $NaHCO_3$, and extracted with EtOAc (4 × 20 mL). The extraction was done with warm solvents to encourage the removal of the water-soluble **18**. The organic layer was dried over anhyd $MgSO_4$ and concentrated to give a viscous, colorless liquid, which was purified by silica gel column chromatography (5:95 MeOH/EtOAc) to give 4.00 g (80%) of a viscous liquid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 10.17 (s, 1H), 4.37 (t, J = 5.0 Hz, 2H), 3.40−3.33 (m, 4H), 2.20 (t, J = 8.0 Hz, 2H), 2.11−2.08 (t, J = 7.0 Hz, 2H),

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1.46−1.39 (m, 8H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 159.0, 60.93, 60.91, 33.6, 33.1, 32.6, 27.0, 22.9, 22.2. IR (liquid film) 3400 (s), 1645 (s) cm^{-1}. HRMS-ESI calcd for $C_9H_{19}NO_3Na$ 212.1263; found 212.1255.

***N*-(2-Methoxyethoxy)-2,5,15,18-tetraoxanonadecan-10-one Oxime (20).** 1,9-Dihydroxynonan-5-one oxime (**18**, 1.50 g, 7.93 mmol) in 20 mL of THF was added dropwise at 0 °C to a solution of NaH (60% in mineral oil, 1.40 g, 35.0 mmol) in 30 mL of THF, and the resulting mixture was stirred for 30 min. To this was added 2-methoxyethyl tosylate[50] (7.80 g, 33.9 mmol) in 20 mL of THF dropwise at 0 °C. Then the reaction mixture was refluxed for 12 h with constant stirring. The reaction mixture was cooled to rt, and MeOH was added dropwise to destroy the excess NaH. The mixture was rotary evaporated, and the resulting crude product was extracted with ether. The organic layer was concentrated to give a yellowish liquid, which then was column chromatographed over silica gel eluting with EtOAc to give 0.70 g (39%) of pure product as an oily liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.14 (t, J = 4.8 Hz, 2H), 3.62−3.53 (m, 10H), 3.48 (t, J = 6.6 Hz, 4H), 3.40 (s, 6H), 3.39 (s, 3H), 2.32 (t, J = 7.5 Hz, 2H), 2.17 (t, J = 7.2 Hz, 2H), 1.64−1.51 (m+t, J = 7.8 Hz, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.3, 72.5, 72.1, 71.3, 71.27, 71.24, 70.2, 70.1, 59.2, 59.1, 33.9, 29.8, 29.4, 27.9, 23.2, 22.6. IR (liquid film) 1635 (w), 1456 (m) cm^{-1}. HRMS (TOF MS ES$^+$) calcd for $C_{18}H_{37}NO_6Na$ 386.2519; found 386.2520.

2,5,15,18-Tetraoxanonadecan-10-amine (13c). Compound **18** (700 mg, 1.93 mmol) was dissolved in THF on ice with constant stirring. To this was added LAH (150 mg, 3.95 mmol), and the reaction mixture was stirred for 10 min on ice and 2 d at reflux. The LAH was quenched with EtOAc and then 10% NaOH, and the resulting mixture was stirred for 20 min. The reaction mixture was then filtered and extracted with EtOAc to give a colorless viscous liquid, which was purified by silica gel column chromatography to give 0.35 g (62%) of pure product as an oily liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60−3.54 (m, 8H), 3.50 (t, J = 6.3 Hz, 4H), 3.39 (s, 6H), 3.19 (s, 2H+H_2O) 2.85 (m, 1H), 1.66−1.54 (m, 4H), 1.51−1.41 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 71.9, 71.3, 69.9, 59.0, 51.0, 37.7, 29.6, 22.6. IR (liquid film) 3369 (s), 1592 (m) cm^{-1}. HRMS (TOF MS ES$^+$) calcd for $C_{15}H_{33}NO_4Na$ 314.2307; found 314.2283.

***N*,*N*′-Di[10-(2,5,15,18-tetraoxanonadecyl)]perylene-3,4,9,10-bis(dicarboximide) (6c).** A mixture of **13c** (4.00 g, 13.7 mmol), 3,4,9,10-perylenetetracarboxylic dianhydride (**5**, 2.50 g, 6.37 mmol), imidazole (10.0 g), and a catalytic amount of $Zn(OAc)_2$ (127 mg) was heated at 165 °C for 8 h. The reaction mixture solidified upon cooling and was dissolved in CH_2Cl_2 and washed with 5% HCl (aq) followed by brine solution. The organic layer was dried over anhyd $MgSO_4$, concentrated, and purified by neutral Al_2O_3 column chromatography ($CHCl_3$) followed by flash column chromatography over silica gel (1:9 MeOH/CH_2Cl_2) to give 3.51 g (59%) of pure product as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59−8.44 (m, 8H), 5.21−5.16 (m, 2H), 3.51−3.40 (m, 24H), 3.29 (s, 12H), 2.35−2.22 (m, 4H), 1.94−1.84 (m, 4H), 1.65−1.69 (m, 8H), 1.44−1.34 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 163.3, 134.2, 131.6, 130.9, 129.3, 126.1, 123.6, 122.9, 122.8, 71.8, 71.1, 69.8, 58.9, 54.3, 32.0, 29.3, 23.4. IR (KBr pellet) 1697 (s), 1655 (s), 1595 (w) cm^{-1}. HRMS (TOF MS ES$^+$) calcd for $C_{54}H_{70}N_2O_{12}Na$ 961.4827; found 961.4847.

***N*-[10-(2,5,15,18-Tetraoxanonadecyl)]-3,4,9,10-perylenetetracarboxylic Acid 3,4-Anhydride 9,10-Imide (7c).** A solution of **6c** (500 mg, 0.532 mmol) in EtOH was treated with KOH as follows, with monitoring by TLC. First 124 mg of KOH (2.21 mmol) was added while the reaction was heated at 55 °C for 1 h, then 240 mg of KOH (4.28 mmol) at 65 °C for 2 h, and finally 250 mg of KOH (4.46 mmol) at 75 °C for 2 h. The reaction mixture was then cooled to rt, acidified with 5% HCl and extracted with $CHCl_3$. The organic layer was treated with brine, dried over anhyd $MgSO_4$, and concentrated to give a solid. This was purified by silica gel column chromatography (5:95 MeOH/$CHCl_3$) to give 220 mg (62%) of pure product as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69−8.62 (m, 8H), 5.22 (m, 1H), 3.54−3.42 (m, 12H), 3.33 (s, 6H), 2.32−2.28 (m, 2H), 1.91−1.87 (m, 2H), 1.69−1.60 (m, 4H+H_2O), 1.49−1.24 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 162.9, 135.3, 134.1, 131.2, 123.3, 123.0, 71.8, 71.2, 69.9, 59.0, 54.5, 32.1, 29.4, 23.5. HRMS (TOF MS ES$^+$) calcd for $C_{39}H_{39}NO_9Na$ 688.2523; found 688.2545.

Methyl 13-Bromo-2-(9-bromononyl)-3-oxotridecanoate (22). A solution of 11-bromo undecanoic acid (**21**) (24.7 g, 93.0 mmol) and concd H_2SO_4 (5 mL) in MeOH (300 mL) was refluxed for 4 h. After most of the solvent was removed under reduced pressure, water was added, and the mixture was extracted with ether. The ether layer was washed with 5% $NaHCO_3$, water, and brine, dried over anhyd $MgSO_4$, and concentrated by rotary evaporation to yield 20.9 g (80.0%) of crude methyl undecanoate,[51] which was used without purification in the next step. ^{1}H NMR was in agreement with the literature.[52]

$TiCl_4$ (8.07 g, 42.5 mmol) in toluene (50 mL) was added to a stirred solution of methyl undecanoate (7.92 g, 28.4 mmol) and Bu_3N (9.46 g, 51.1 mmol) in toluene at −78 °C. After 1 h, the mixture was raised to rt and stirred overnight. It was then quenched with water and extracted twice with ether. The combined organic phase was washed with water and brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The resulting crude oil was purified by silica gel chromatography (98:2 hexane/EtOAc) to give 8.3 g (56%) of **22** as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.70 (s, 3H), 3.44−3.36 (m+t, J = 6.0 Hz, 5H), 2.56−2.39 (m, 2H), 1.86−1.79 (m, 6H), 1.57−1.53 (m, 2H), 1.42−1.38 (m, 4H), 1.26 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.3, 170.3, 58.9, 52.2, 41.8, 33.9, 33.9, 32.7, 32.7, 29.3, 29.29, 29.28, 29.26, 29.25, 29.1, 28.7, 28.6, 28.12, 28.10, 23.4. IR 2987, 2854, 1745, 1716. HRMS (TOF MS ES$^+$) calcd for $C_{23}H_{42}Br_2O_3Na$ 547.1398; found 547.1407.

1,21-Dibromoheneicosan-11-one (23). To a mixture of **22** (2.04 g, 3.88 mmol) in 60 mL of diethyl ether was added 10 mL of satd NaOH (aq), and the mixture was refluxed overnight. The solvent was removed under reduced pressure, and the aqueous layer was extracted several times with ether. The organic layer was washed several times with water and dried over anhyd $MgSO_4$, and the solvent was removed under reduced pressure to yield 1.5 g of crude powder, which was purified by silica gel chromatography (97:3 hexane/EtOAc) to give 1.1 g (65%) as a white solid, mp 50−53 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.40 (t, J = 6.0 Hz, 4H), 2.40−2.36 (m, 4H), 1.87−1.80 (m, 4H), 1.58−1.53 (m, 4H), 1.44−1.39 (m, 4H), 1.27 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.5, 42.7, 33.9, 32.8, 29.35, 29.32, 29.2, 28.7, 28.1, 23.8. HRMS (TOF MS ES$^+$) calcd for $C_{21}H_{40}Br_2ONa$ 489.1344; found 489.1347.

1,21-Dihydroxyheneicosan-11-one (24). A mixture of **23** (0.98 g, 2.09 mmol) and potassium acetate (616 mg, 6.28 mmol) in DMF (15 mL) was stirred for 2 h at 60 °C under nitrogen. Solvent was removed under reduced pressure to obtain crude diacetoxy ketone as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.05 (t, J = 9.0, 4H), 2.38 (t, J = 6.0 Hz, 4H), 2.04 (s, 6H), 1.61−1.30 (m, 8H), 1.27 (m, 24H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.5, 171.1, 64.6, 42.7, 29.4, 29.37, 29.34, 29.2, 29.1, 28.5, 25.8, 23.8, 20.9. HRMS (TOF MS ES$^+$) calcd for $C_{25}H_{46}O_5Na$ 449.3243; found 449.3221.

Crude diacetoxy ketone was treated with KOH (700 mg) in methanol (20 mL) at 60 °C. The mixture was concentrated and extracted with dichloromethane. The extract was washed twice with water and dried over $MgSO_4$. Evaporation of solvent gave pure product as a white solid (0.40 g, 45%), which was used without purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.66 (t, J = 6.0 Hz, 4H), 2.40 (t, J = 9.0, 4H), 1.63−1.54 (m, 10H), 1.29 (m, 24H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.7, 63.0, 42.8, 32.7, 29.5, 29.3, 29.2, 25.7, 23.8. HRMS (TOF MS ES$^+$) calcd for $C_{21}H_{42}O_3Na$ 365.3032; found 365.3055.

11-Aminoheneicosane-1,21-diol (13d). To a solution of **24** (3.57 g, 10.4 mmol) in 150 mL of isopropyl alcohol were added NH_4OAc (8.03 g, 104 mmol), $Na(BH_3)CN$ (655 mg, 10.4 mmol) and crushed 4 Å molecular sieves in one portion under nitrogen, and the mixture was stirred for 36 h at rt. The crushed molecular sieves were removed via vacuum filtration, and water was added to the filtrate, which was extracted twice with diethyl ether. The organic layer was washed with 1 M NaOH and brine and dried over anhyd $MgSO_4$ to obtain a brown oil after concentration, which was purified by silica gel chromatography (3:1:1 hexane/EtOAc/MeOH) to obtain 2.4 g of **13d**

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(69%) as a white solid, mp 99−100 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68−3.64 (m, 4H), 2.68 (m, 1H), 1.61−1.54 (m, 6H), 1.34−1.30 (m, 34H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 62.9, 51.3, 36.6, 32.7, 29.7, 29.6, 29.4, 29.38, 29.32, 25.8, 25.7. HRMS (TOF MS ES$^+$) calcd for $C_{21}H_{45}NO_2Na$ 366.3348; found 366.3371.

***N*,*N*′-Bis(1,21-dihydroxyheneicos-11-yl)perylene-3,4,9,10-bis(dicarboximide) (6d).** A mixture of 1.14 g (2.91 mmol) of **5**, 2.2 g (6.4 mmol) of **13d**, 5 g of imidazole, and a catalytic amount of zinc acetate was heated with stirring at 130 °C for 6 h. The mixture was then cooled, dissolved in $CHCl_3$, and directly purified by column chromatography on silica gel ($CHCl_3$) to give 1.6 g (55%) of a deep red, waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68−8.58 (m, 8H), 5.19 (m, 2H), 3.61 (t, J = 6.0 Hz, 8H), 2.30−2.23 (m, 4H), 1.92−1.83 (m, 4H), 1.55−1.48 (m, 12H), 1.30−1.23 (m, 56H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 163.5, 134.5, 131.9, 131.1, 129.5, 126.4, 123.8, 123.0, 63.0, 54.7, 32.7, 32.3, 29.49, 29.46, 29.42, 29.3, 26.9, 25.6. HRMS (TOF MS ES$^+$) calcd for $C_{66}H_{94}N_2O_8Na$ 1065.6908; found 1065.6935.

***N*-(1,21-Dihydroxyheneicos-11-yl)-3,4,9,10-perylenetetracarboxylic Acid 3,4-Anhydride 9,10-Imide (7d).** A mixture of 600 mg (0.57 mmol) of **6d**, 97.0 mg (1.75 mmol) of 85% KOH pellets, and 15 mL of *t*-BuOH was brought to reflux. After 1 h an additional 4 pellets of KOH were added, and heating was continued for an additional 1 h. The reaction was monitored with TLC and stopped after appropriate conversion had occurred. The mixture was poured, with stirring, into a mixture of AcOH and 2 N HCl. The resulting solution was extracted with chloroform, washed twice with water and brine, and purified by silica gel chromatography using 19:1 $CHCl_3$/MeOH to obtain 178 mg (43%) of monoimide **7d** as a waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74−8.68 (m, 8H), 5.24−5.17 (m, 1H), 3.64−3.62 (m, 4H), 2.28−2.25 (m, 2H), 1.89−1.86 (m, 2H), 1.58−1.35 (m, 6H), 1.34−1.25 (m, 28H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 163.3, 159.9, 135.2, 133.6, 133.5, 131.8, 131.1, 129.5, 126.8, 126.5, 124.6, 123.9, 123.1, 119.0, 63.0, 54.9, 32.7, 32.3, 29.48, 29.45, 29.42, 29.3, 26.9, 25.6. HRMS (TOF MS ES$^+$) calcd for $C_{45}H_{51}NO_7Na$ 740.3563; found 740.3589.

***N*-(1,21-Diacetylthioheneicos-11-yl)- 3,4,9,10-perylenetetracarboxylic Acid 3,4-Anhydride 9,10-Imide (7e).** *Method A.* Diol monoimide **7d** (50.2 mg, 0.070 mmol) was dissolved in 4 mL of pyridine, and the reaction mixture was cooled to 0 °C. Tosyl chloride (29.3 mg, 0.154 mmol) dissolved in pyridine was added dropwise at 0 °C, and the reaction mixture was stirred overnight at rt. When TLC showed no starting material left, the reaction mixture was diluted with CH_2Cl_2, washed with water and then brine, dried over anhyd $MgSO_4$, and concentrated by rotary evaporation to obtain 60.7 mg of crude ditosylate monoimide that was used further without purification.

Ditosylate monoimide (50.3 mg, 0.049 mmol) and KSAc (13.9 mg, 0.123 mmol) were dissolved in 5 mL of DMF and stirred overnight at 120 °C. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2, washed with water and then brine, and dried over anhyd $MgSO_4$. After rotary evaporation, the residue was purified by silica gel chromatography (1:99 MeOH/$CHCl_3$) to yield 22 mg (54%) of pure **7e** as a waxy solid.

Method B. Diene monoimide **7h** (417 mg, 0.61 mmol) was dissolved in 20 mL of toluene. To this solution were added thiolacetic acid (0.17 mL, 2.4 mmol) and a catalytic amount of AIBN. The solution was then refluxed for 1 h. The reaction was quenched by addition of 1 M $NaHCO_3$ and extracted with $CHCl_3$. The organic layer was washed three times with 1 M $NaHCO_3$ and then brine, concentrated under reduced pressure, and purified by silica gel chromatography (1:99 MeOH/$CHCl_3$) to yield 428 mg (84%) of pure **7e** as a waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78−8.52 (m, 8H), 5.22−5.16 (m, 1H), 2.82 (t, J = 10.0 Hz, 4H), 2.30 (s+m, 6H + 2H), 1.89 (m, 2H), 1.53−1.50 (m, 4H) 1.35−1.22 (m, 28H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.9, 164.2, 163.1, 159.7, 136.1, 133.3, 131.8, 131.6, 131.1, 129.3, 129.5, 126.3, 124.7, 124.0, 123.8, 123.0, 118.8, 54.9, 32.3, 30.6, 29.49, 29.47, 29.44, 29.3, 29.1, 29.0, 28.7, 26.9. HRMS (TOF MS ES$^+$) calcd for $C_{49}H_{55}NO_7S_2Na$ 856.3318; found 856.3337.

***N*-(1,21-Dimercaptoheneicos-11-yl)-3,4,9,10-perylenetetracarboxylic Acid 3,4-Anhydride 9,10-Imide (7f).** Dithioacetate monoimide **7e** (108 mg, 0.129 mmol) was deprotected by addition of acetyl chloride (2 mL) at 0 °C to a solution in methanol (2 mL) and dichloromethane (10 mL). After overnight stirring at rt the solvent was removed in vacuum, and the residue was dissolved in 20 mL of $CHCl_3$. The solution was washed with 5% $NaHCO_3$, dried over $MgSO_4$, concentrated under reduced pressure, and purified by silica gel chromatography (1:99 MeOH/$CHCl_3$) to yield 92 mg (95%) of pure **7f** as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75−8.69 (m, 8H), 5.23−5.18 (m, 1H), 2.53−2.48 (q, J = 9.0 Hz 4H), 2.30−2.24 (m, 2H), 1.87−1.82 (m, 2H), 1.59−1.55 (m, 4H), 1.36−1.24 (m, 30H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 163.1, 159.6, 136.0, 133.3, 133.2, 131.7, 131.5, 131.0, 130.0, 129.2, 126.4,126.2, 124.7, 123.8, 122.9, 122.0, 121.6, 118.7, 54.9, 34.0, 32.3, 29.5, 29.49, 29.48, 29.43, 29.0, 28.3, 26.9, 24.6. HRMS (TOF MS ES$^+$) calcd for $C_{45}H_{51}NS_2O_5Na$ 772.3106; found 772.3124.

***N*-(1,21-Bis(methyldisulfanyl)heneicos-11-yl)-3,4,9,10-perylenetetracarboxylic Acid 3,4-Anhydride 9,10-Imide (7g).** To a solution of **7f** (47 mg, 0.063 mmol) in CH_2Cl_2 was added methyl methanethiosulfonate (MMTS) (17.7 μL, 0.188 mmol) and triethylamine (26.2 μL, 0.188 mmol) at room temperature. After 5 h of stirring, the reaction mixture was washed with 5% HCl, water, and brine, dried over $MgSO_4$, concentrated under reduced pressure, and purified by silica gel chromatography (1:99 MeOH/$CHCl_3$) to give 92 mg (95%) of pure **7g** as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67−8.50 (m, 8H), 5.22−5.16 (m, 1H), 2.66 (t, J = 9.0 Hz, 4H), 2.38 (s, 6H), 2.32−2.26 (m, 2H), 2.24−2.21 (m, 2H), 1.94−1.85 (m, 4H), 1.69−1.23 (m, 28H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 163.1, 159.7, 136.1, 133.3, 131.8, 131.5, 131.1, 129.3, 126.4, 126.2, 123.8, 123.0, 118.7, 54.9, 38.3, 32.3, 29.5, 29.47, 29.45, 29.41, 29.1, 28.4, 26.9, 23.3. HRMS (TOF MS ES$^+$) calcd for $C_{47}H_{55}NO_5S_4Na$ 864.2861; found 864.2869.

Methyl 2-(Non-8-enyl)-3-oxotridec-12-enoate (26). A solution of 11-undecenoic acid (**25**) (45.7 g, 248 mmol) and concd H_2SO_4 (5 mL) in MeOH (600 mL) was refluxed for 6 h. After most of the solvent was removed under reduced pressure, water was added, and the mixture was extracted with ether. The ether layer was washed with 5% $NaHCO_3$, water, and brine, dried over anhyd $MgSO_4$, and concentrated by rotary evaporation to yield 45 g (92%) of crude methyl undecanoate, which was used without purification in the next step. ^{1}H NMR was in agreement with the literature.[52]

$TiCl_4$ (6.11 g, 32.2 mmol) in toluene (50 mL) was added to a stirred solution of methyl undecanoate (5.16 g, 17.9 mmol) and Bu_3N (4.98 g, 26.9 mmol) in toluene at 0−5 °C. After 1 h, the mixture was raised to rt and stirred overnight. It was then quenched with water and extracted twice with ether. The combined organic phase was washed with water and brine, dried over $MgSO_4$, and concentrated by rotary evaporation. The resulting crude oil was purified by silica gel chromatography (98:2 hexane/EtOAc) to give 7.0 g (74%) of **26** as an oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85−5.76 (m, 2H), 5.03−4.91 (m, 4H), 3.72 (s, 3H), 3.46−3.41 (m, 1H), 2.54−2.46 (m, 2H), 2.07−2.00 (m, 4H), 1.84−1.60 (m, 2H), 1.57−1.32 (m, 2H), 1.28−1.24 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.4, 170.4, 139.1, 139.0, 114.16, 114.13, 58.9, 52.2, 41.8, 33.78, 33.75, 29.35, 29.31, 29.2, 29.1, 29.04, 29.00, 28.9, 28.88, 28.83, 28.2, 27.4, 23.4. IR 2927, 2855, 1747, 1717. HRMS (TOF MS ES$^+$) calcd for $C_{23}H_{40}O_3Na$ 387.2875; found 387.2898.

Heneicosa-1,20-dien-11-one (27). To a solution of **26** (4.0 g, 7.6 mmol) in 100 mL of THF was added 20 mL of satd NaOH (aq), and the mixture was refluxed overnight. The solvent was removed under reduced pressure, and the aqueous layer was extracted several times with ether. The organic layer was washed several times with water and dried over anhyd $MgSO_4$, and the solvent was removed under reduced pressure to yield 3.0 g of crude powder, which was purified by silica gel chromatography (97:3 hexane/EtOAc) to give 2.83 g (84%) of **27**, mp 55−56 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87−5.81 (m, 2H), 5.03−4.94 (m, 4H), 2.43−2.39 (m, 4H), 2.08−2.04 (m, 4H), 1.60−1.58 (m+s, 6H + H_2O), 1.39−1.38 (m, 4H), 1.30 (m, 14H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.8, 139.2, 114.1, 42.8, 33.8, 29.38, 29.33, 29.2, 29.0, 28.9, 23.8. IR 1698, 994, 915. HRMS (TOF MS ES$^+$) calcd for $C_{21}H_{38}ONa$ 329.2820; found 329.2790.

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Heneicosa-1,20-dien-11-amine (13h). To a solution of **27** (5.06 g, 16.5 mmol) in 150 mL of isopropyl alcohol were added NH_4OAc (12.7 g, 165 mmol), $Na(BH_3)CN$ (1.03g, 16.5 mmol), and crushed 4 Å molecular sieves in one portion under nitrogen, and the mixture was stirred for 36 h at rt. The crushed molecular sieves were removed via vacuum filtration, and deionized water was added to the filtrate, which was extracted twice with diethyl ether. The organic layer was washed with 1 M NaOH and brine and dried over anhyd $MgSO_4$ to obtain a brown oil after concentration, which was purified by silica gel chromatography (3:1:1 hexane/EtOAc/MeOH) to obtain 3.7 g of **13h** (73%) as a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.89−5.76 (m, 2H), 5.04−4.92 (m, 4H), 2.69−2.67 (m, 1H), 2.09−2.02 (m, 4H), 1.41−1.38 (m, 10H), 1.36−1.21 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 114.1, 51.2, 37.3, 33.8, 29.7, 29.5, 29.4, 29.1, 28.9, 26.0. HRMS (TOF MS ES$^+$) calcd for $C_{21}H_{41}NNa$ 330.3137; found 330.3166.

***N*,*N*′-Di(1,20-heneicosadien-11-yl)perylene-3,4,9,10-bis-(dicarboximide) (6h).** A mixture of 3.07 g (7.83 mmol) of **5**, 5.06 g (16.4 mmol) of **13h**, 15 g of imidazole, and a catalytic amount of zinc acetate was heated with stirring at 160 °C for 2 h. The mixture was then cooled, dissolved in $CHCl_3$, and directly purified by column chromatography on silica gel ($CHCl_3$) to give 3.9 g (74%) of a deep red, waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70−8.64 (m, 8H), 5.84−5.70 (m, 4H) 5.19 (m, 2H), 4.98−4.87 (m, 8H), 2.25 (m, 4H), 2.03−1.95 (m, 8H), 1.87 (m, 4H), 1.32−1.23 (m, 48H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.6, 163.5, 139.2, 134.4, 131.8, 131.1, 129.5, 126.4, 123.9, 123.0, 114.0, 54.7, 33.7, 32.3, 29.5, 29.4, 29.08, 29.01, 28.8, 26.9. HRMS (TOF MS ES$^+$) calcd for $C_{66}H_{86}N_2O_4Na$ 993.6485; found 993.6491.

***N*-(1,20-Heneicosadien-11-yl)-3,4,9,10-perylenetetracarboxylic Acid 3,4-Anhydride-9,10 Imide (7h).** A mixture of 1.24 g (1.27 mmol) of **6h**, 215 mg (3.83 mmol) of 85% KOH pellets, and 50 mL of *t*-BuOH was brought to reflux. After 1 h an additional 10 pellets of KOH were added, and heating was continued for an additional 1 h. The reaction was monitored with TLC and stopped after appropriate conversion had occurred. The mixture was poured with stirring into a mixture of 70 mL of AcOH and 40 mL of 2 N HCl. The resulting solution was extracted with chloroform, which was washed twice with water and once with brine, concentrated, and purified by silica gel chromatography using $CHCl_3$ to obtain 520 mg (59%) of monoimide **7h** as a waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66−8.46 (m, 8H), 5.84−5.70 (m, 2H), 5.22−5.13 (m, 1H), 4.98−4.87 (m, 4H), 2.27−2.01 (m, 2H), 1.98−1.89 (m+m, 2H+4H), 1.37−1.25 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.3, 163.2, 159.8, 139.1, 136.2, 133.4, 131.7, 129.4, 126.6, 126.4, 123.8, 123.0, 118.9, 114.0, 54.8, 33.7, 32.2, 29.46, 29.42, 29.3, 29.06, 29.03, 28.8, 26.9. HRMS (TOF MS ES$^+$) calcd for $C_{45}H_{47}NO_5Na$ 704.3352; found 704.3381.

General Procedure for Bisimide D-σ-A Molecules with a PEG Swallowtail (R = b). Perylene monoimide monoanhydride with a PEG swallowtail (**7b**) and a suitable donor amine were added to pyridine and stirred under reflux for 12 h. Then the reaction mixture was added to excess 5% HCl and extracted with $CHCl_3$. The organic layer was then washed with an excess of 10% K_2CO_3, dried over anhyd Na_2SO_4, and rotary evaporated to give crude product, which was purified by silica gel chromatography. Pyrenemethylamine (**1-NH$_2$**) was prepared by treating pyrenemethylammonium chloride (Aldrich) with KOH (aq) and MeOH.

***N*-(2,5,8,12,15,18-Hexaoxanonadec-10-yl)-*N*′-(1-pyrenylmethyl)perylene-3,4,9,10-bis(dicarboximide) (1b).** Prepared from **7b** (98.0 mg, 0.146 mmol) and 1-pyrenylmethylamine (**1-NH$_2$**, 43.0 mg, 0.186 mmol). Elution with 99:1 $CHCl_3$/MeOH gave 25 mg (19%) of **1b** as a waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64−8.14 (m, 5H), 8.11−8.07 (d, 4H), 8.05−7.82 (m, 8H), 6.11 (s, 2H), 5.74−5.72 (m, 1H), 4.27−4.21 (m, 2H), 4.04−3.99 (m, 2H), 3.77−3.57 (m, 12H), 3.46−3.43 (m, 4H), 3.30 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.5, 163.3, 133.8, 133.4, 131.0, 130.6, 130.2, 129.9, 128.6, 128.5, 128.3, 127.5, 126.8, 126.7, 125.5, 125.4, 125.3, 125.2, 124.9, 124.8, 124.5, 124.2, 124.0, 122.8, 122.4, 122.2, 71.8, 70.5, 70.4, 70.3, 69.4, 58.9, 52.1, 41.2. IR (KBr) 1692 (s), 1656 (s), 1595 (s), 1341 (s), 1252 (m), 1110 (s) cm^{-1}. HRMS (TOF MS ES$^+$) calcd for $C_{54}H_{46}N_2O_{10}Na$ 905.3050; found 905.3077.

***N*-(2,5,8,12,15,18-Hexaoxanonadec-10-yl)-*N*′-(4-[1-pyrenyl]-butyl)perylene-3,4,9,10-bis(dicarboximide) (2b).** Prepared from **7b** (102 mg, 0.152 mmol) and 4-pyrenylbutylamine (**2-NH$_2$**, Toronto Research Chemicals, 52.0 mg, 0.190 mmol). Elution with 99:1 $CHCl_3$/MeOH gave 26 mg (18%) of **2b** as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37−8.21 (m, 4H), 8.08−7.62 (m, 13H), 5.78−5.72 (m, 1H), 4.31−4.20 (m, 4H), 4.08−4.02 (m, 2H), 3.85−3.59 (m, 12H), 3.47 (t, J = 6.0 Hz, 4H), 3.31 (s, 6H), 3.14 (m, 2H), 1.95 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ163.7, 163.0, 136.1, 133.8, 133.7, 130.9, 130.7, 130.3, 129.3, 128.4, 128.0, 127.3, 127.1, 126.8, 126.1, 125.4, 124.5, 124.4, 124.3, 123.0, 122.4, 122.3, 71.8, 70.5, 70.4, 70.3, 69.4, 58.9, 52.0, 40.2, 33.3, 28.8, 27.8. IR (KBr) 1692 (s), 1655 (s), 1595 (m), 1342 (s), 1253 (m), 1109 (s) cm^{-1}. HRMS (TOF MS ES$^+$) calcd for $C_{57}H_{52}N_2O_{10}Na$ 947.3520; found 947.3517.

***N*-(2-Ferrocenylethyl)-*N*′-(2,5,8,12,15,18-hexaoxanonadec-10-yl)perylene-3,4,9,10-bis(dicarboximide) (3b).** Prepared from **7b** (119 mg, 0.178 mmol) and 3-ferrocenylethylamine[1] (**3-NH$_2$**, 51 mg, 0.22 mmol). Elution with 99.4:0.6 $CHCl_3$/MeOH gave 47 mg (24%) of **3b** as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.59−8.51 (m, 4H), 8.44−8.39 (m, 4H), 5.77−5.68 (q, 1H), 4.37 (m, 2H), 4.22 (m, 9H), 4.10 (s, 2H), 3.65 (m, 2H), 3.63−5.56 (m, 12H), 3.45−3.44 (m, 4H), 3.28 (s, 6H), 2.82−2.77 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 163.1, 134.4, 134.1, 131.2, 129.3, 129.1, 126.2, 126.0, 123.4, 123.0, 122.96, 122.92, 85.1, 71.8, 70.5, 70.4, 70.3, 68.6, 58.9, 52.1, 41.2, 27.7. IR (KBr) 1696 (s), 1655 (s), 1596 (m), 1342 (s), 1249 (m), 1105 (s) cm^{-1}. HRMS (TOF MS ES$^+$) calcd for $C_{49}H_{48}FeN_2O_{10}Na$ 903.2557; found 903.2574.

***N*-(3-[2,5-Bis(dimethylamino)phenyl]propyl)-*N*′-(2,5,8,12,15,18-hexaoxanonadec-10-yl)perylene-4,5,9,10-bis-(dicarboximide) (4b).** Prepared from **7b** (126 mg, 0.188 mmol) and 3-tetramethylphenylenediaminylpropylamine[1] (**4-NH$_2$**, 70.0 mg, 0.316 mmol). Elution with 49:1 $CHCl_3$/MeOH gave 21 mg (13%) of **4b** as a waxy solid and 50 mg (31%) of an additional fraction containing a trace impurity by TLC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57−8.51 (m, 4H), 8.42−8.35 (m, 4H), 7.05−7.03 (d, 1H), 6.71 (s, 1H), 6.56−6.55 (d, 1H), 5.75−5.69 (m, 1H), 4.32−4.30 (m, 2H), 4.20−4.23 (m, 2H), 3.97−4.01 (m, 2H), 3.64−3.57 (m, 12H), 3.44−3.42 (m, 4H), 3.28 (s, 6H), 2.89 (s, 8H), 2.62 (s, 6H) 2.19−2.13 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 163.0, 147.5, 143.1, 137.4, 134.0, 131.0, 129.2, 128.9, 125.9, 125.8, 123.2, 123.1, 122.8, 122.7, 120.6, 114.2, 111.3, 71.8, 70.5, 70.4, 70.3, 69.3, 58.9, 52.1, 45.8, 41.1, 40.9, 29.7, 28.6. IR (KBr) 1698 (s), 1655 (s), 1596 (m), 1343 (s), 1107 (s) cm^{-1}. HRMS (TOF MS ES$^+$) calcd for $C_{50}H_{56}N_4O_{10}Na$ 895.3894; found 895.3890.

General Procedure for Bisimides D-σ-A Molecules with a Mixed Swallowtail (R = c). Perylene monoimide monoanhydride with a mixed alkyl-PEG swallowtail **7c** and a donor amine were dissolved in toluene and refluxed for 12 h to give the target nonsymmetric bisimides **1c**−**4c**. These were purified by neutral Al_2O_3 column chromatography ($CHCl_3$) followed by silica gel column chromatography (99:1 $CHCl_3$/MeOH).

***N*-(1-Pyrenylmethyl)-*N*′-(2,5,15,18-tetraoxanonadec-10-yl)-perylene-3,4,9,10-bis(dicarboximide) (1c).** Pyrenylmethylamine **1-NH$_2$** (35 mg, 0.15 mmol) and **7c** (70.0 mg, 0.105 mmol) gave 30 mg (27%) of **1c** as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41−8.35 (d, J = 9.4 Hz, 3H), 8.16−8.13 (d, J = 7.9 Hz, 2H), 7.95 (d, J = 7.9 Hz, 2H), 7.74 (m, 8H), 7.54 (m, 2H), 5.86 (s, 2H), 5.23 (m, 1H), 3.47 (m, 12H), 3.31 (s, 6H), 2.34 (m, 2H), 1.99 (m, 2H), 1.68 (m, 4H), 1.46 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 163.2, 133.6, 133.3, 130.7, 130.6, 130.18, 130.15, 129.9, 128.7, 128.3, 127.4, 126.7, 125.6, 125.5, 125.2, 125.1, 124.8, 124.7, 124.4, 124.2, 123.9, 122.8, 122.6, 122.4, 122.2, 122.0, 71.8, 71.2, 69.8, 58.9, 54.5, 41.1, 32.2, 29.5, 23.6. IR (KBr) 1692 (s), 1655 (s), 1595 (s) cm^{-1}. HRMS (TOF MS ES$^+$) calcd for $C_{56}H_{50}N_2O_8Na$ 901.3465; found 901.3491.

***N*-[4-(1-Pyrenyl)butyl]-*N*′-(2,5,15,18-tetraoxanonadec-10-yl)-perylene-3,4,9,10-bis(dicarboximide) (2c).** Pyrenebutylamine (**2-NH$_2$**, 15 mg, 0.056 mmol) and **7c** (25 mg, 0.038 mmol) gave 7.5 mg (22%) of **2c** as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (m, 2H), 8.45 (dxd, J = 9.0 Hz, 3.0 Hz, 4H), 8.34 (d, J = 9.0 Hz, 2H), 8.14

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(d, J = 9.0 Hz, 1H), 8.00−7.40 (m, 8H), 5.24 (m, 1H), 4.25 (s, 2H), 3.54−3.46 (m, 12H), 3.33 (s, 6H), 2.32−2.34 (m, 2H), 1.94−2.02 (m +m, 2H + 4H), 1.60−1.69 (m, 6H + H_2O), 1.44 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 163.2, 143.4, 136.2, 134.2, 131.0, 130.5, 129.5, 128.3, 127.5, 127.3, 126.9, 126.2, 125.9, 125.5, 124.6, 124.5, 123.2, 122.8, 122.7, 122.6, 71.8, 71.2, 69.9, 59.0, 54.5, 40.3, 33.4, 32.1, 29.4, 28.6, 27.6, 23.5. HRMS (TOF MS ES$^+$) calcd for $C_{59}H_{56}N_2O_8Na$ 943.3934; found 943.3951.

***N*-(2-Ferrocenylethyl)-*N*′-(2,5,15,18-tetraoxanonadec-10-yl)-perylene-3,4,9,10-bis(dicarboximide) (3c).** Ferrocenylethylamine **3-NH$_2$** (62 mg, 0.28 mmol) and **7c** (80 mg, 0.12 mmol) in 5 mL of toluene gave 21 mg (20%) of **3c** as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66−8.55 (m, 8H), 5.21 (m, 1H), 4.43−4.37 (m, 2H), 4.22 (s, 7H), 4.12 (s, 2H), 3.51−3.43 (m, 12H), 3.32 (s, 6H), 2.81−2.76 (m, 2H), 2.32−2.29 (m, 2H), 1.95−1.91 (m, 2H), 1.71−1.66 (m, 4H), 1.65−1.40 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 163.1, 134.6, 134.2, 131.3, 129.4, 126.4, 123.1, 123.06, 123.00, 85.0, 71.8, 71.2, 69.9, 68.6, 68.1, 67.4, 59.0, 54.5, 41.2, 32.1, 29.4, 27.7, 23.5. IR (KBr) 1692 (s), 1656 (s), 1596 (s) cm^{-1}. HRMS (TOF MS ES$^+$) calcd for $C_{51}H_{52}FeN_2O_8Na$ 899.2972; found 899.2991.

***N*-(3-[2,5-Bis(dimethylamino)phenyl]propyl)-*N*′-(2,5,15,18-tetraoxanonadec-10-yl)perylene-4,5,9,10-bis(dicarboximide) (4c).** TMPDA-propanamine **4-NH$_2$** (80.0 mg, 0.361 mmol) and **7c** (120 mg, 0.180 mmol) gave 44 mg (28%) of **4c** as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66−8.56 (m, 8H), 7.06−7.04 (d, J = 6.0 Hz, 1H), 6.72−6.71 (d, J = 3.0 Hz, 1H), 6.58−6.55 (d × d, J = 10 Hz, 5.0 Hz, 1H), 5.23−5.21 (m, 1H), 4.35−4.32 (m, 2H), 3.54−3.45 (m, 12H), 3.33 (s, 6H), 2.90−2.89 (m, 6 + 2H), 2.63 (s, 6H), 2.31 (m, 2H), 2.14 (m, 2H), 1.92 (m, 2H), 1.67 (4H+H_2O), 1.38 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.5, 163.2, 147.5, 137.4, 131.2, 129.3, 126.4, 123.3, 122.98, 122.95, 120.6, 114.2, 111.3, 71.9, 71.2, 69.9, 58.9, 54.5, 45.8, 41.1, 40.8, 32.1, 29.4, 28.6, 23.5. IR (KBr) 1695 (s), 1655 (s), 1595 (s) cm^{-1}. HRMS (TOF MS ES$^+$) calcd for $C_{52}H_{60}N_4O_8Na$ 891.4309; found 891.4333.

General Procedure for Bisimide D-σ-A Molecules with a Dithioacetyl Swallowtail (R = e). A mixture of the perylene monoimide monoanhydride with a dithioacetylalkyl swallowtail (**7e**) and a 2- to 4-fold molar excess of the appropriate amine was refluxed in toluene for 1−2 h. The reaction mixture was then cooled, washed with 5% HCl followed by 10% K_2CO_3, dried over $MgSO_4$, and concentrated by rotary evaporation. Crude products were purified by chromatography on silica gel (1:99 MeOH/$CHCl_3$) to give red solids. Melting points were difficult to obtain due to the deep color and waxy nature of the materials.

***N*-(1,21-Diacetylthioheneicos-11-yl)-*N*′-([1-pyrenyl]methyl)-perylene-3,4,9,10-bis(dicarboximide) (1e). 1-NH$_2$** (20.7 mg, 0.090 mmol) and **7h** (47.0 mg, 0.045 mmol) gave 33 mg (88%) of pure **1e** as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68−8.61 (m, 5H), 8.53−8.47 (m, 4H), 8.19−8.04 (m, 5H), 7.97−7.90 (m, 3H), 6.12 (s, 2H), 5.20 (m, 1H), 2.81 (t, J = 6.0 Hz, 4H), 2.30−2.25 (s+m, 6H + 2H), 1.88−1.85 (m, 2H), 1.53−1.45 (m, 4H), 1.30−1.19 (m, 28H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.2, 164.8, 163.7, 134.7, 134.1, 131.6, 131.3, 130.8, 130.8, 130.3, 129.5, 129.3, 128.9, 127.9, 127.4, 127.3, 126.2, 126.2, 126.0, 125.3, 125.2, 124.9, 124.8, 124.7, 124.1, 123.3, 123.2, 122.9, 55.0, 41.6, 32.6, 30.8, 29.79, 29.75, 29.72, 29.6, 29.38, 29.31, 29.2, 29.0, 27.2. HRMS (TOF MS ES$^+$) calcd for $C_{66}H_{66}N_2O_6S_2Na$ 1069.4260; found 1069.4248.

***N*-(1,21-Diacetylthioheneicos-11-yl)-*N*′-(4-[1-pyrenyl]butyl)-perylene-3,4,9,10-bis(dicarboximide) (2e). 2-NH$_2$** (43.30 mg, 0.158 mmol) and **7e** (66.00 mg, 0.079 mmol) gave **2e** in 82% yield as a waxy solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46−7.52 (m, 17H), 5.26−5.18 (m, 1H), 4.17−4.12 (m, 2H), 3.12−3.07 (m, 2H), 2.81 (t, J = 9.0 Hz, 4H), 2.32−2.27 (s+m 6H + 2H), 1.94−1.91 (m, 4H), 1.55−1.45 (m, 6H), 1.37−1.23 (m, 28H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.0, 164.4, 162.9, 136.1, 133.6, 130.8, 130.5, 130.3, 129.2, 128.9, 128.3, 127.9, 127.2, 127.0, 126.7, 126.0, 125.4, 125.3, 124.5, 124.38, 124.32, 124.2, 122.9, 122.4, 122.2, 122.1, 54.6, 40.1, 33.3, 32.3, 30.5, 29.55, 29.52, 29.48, 29.43, 29.3, 29.07, 29.05, 28.9, 28.7, 27.0. HRMS (TOF MS ES$^+$) calcd for $C_{69}H_{72}N_2O_6S_2Na$ 1111.4729; found 1111.4746.

***N*-(1,21-Diacetylthioheneicos-11-yl)-*N*′-(2-ferrocenylethyl)-perylene-3,4,9,10-bis(dicarboximide) (3e). 3-NH$_2$** (27.50 mg, 0.120 mmol) and **7e** (50.1 mg, 0.06 mmol) gave **3e** (54 mg) in 86% yield as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69−8.53 (m, 8H), 5.23−5.18 (m, 1H), 4.40 (t, J = 6.0 Hz, 2H), 4.23 (s,7H), 4.16 (s, 2H), 2.85−2.76 (m, 6H), 2.31−2.25 (m, 6H + 2H), 1.92−1.85 (m, 2H), 1.60−1.47 (m, 4H), 1.32−1.22 (m, 28H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.0, 164.5, 163.1, 134.6, 134.2, 131.2, 129.4, 129.2, 126.3, 126.2, 123.0, 122.9, 85.0, 68.6, 68.1, 67.4, 54.7, 41.2, 32.3, 30.6, 29.5, 29.46, 29.44, 29.3, 29.1, 29.0, 28.7, 27.7, 26.9. HRMS (TOF MS ES$^+$) calcd for $C_{61}H_{68}FeN_2O_6S_2Na$ 1067.3768; found 1067.3789.

***N*-(1,21-Diacetylthioheneicos-11-yl)-*N*′-(3-[2-(*N*′,*N*′,*N*″,*N*″-tetramethyl-1,4-benzenediaminyl)propyl)perylene-3,4,9,10-bis(dicarboximide) (4e). 4-NH$_2$** (7.96 mg, 0.036 mmol) and **7e** (30.0 mg, 0.036 mmol) gave **4e** (26 mg) in 71% yield as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53−8.46 (m, 2H), 8.31−8.12 (m, 6H), 7.03−7.00 (d, J = 6.0 Hz, 1H), 6.70 (d, J = 3.0 Hz, 1H), 6.54−6.50 (dxd, J = 9.0 Hz, 3.0 Hz, 1H), 5.21−5.14 (m, 1H), 4.25−4.20 (m, 2H), 2.88−2.78 (m, 10H), 2.60 (s, 6H), 2.29−2.28 (m, 8H), 2.16−2.05 (m, 2H), 1.94−1.90 (m, 2H), 1.54−1.42 (m, 6H), 1.37−1.22 (m, 28H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8, 164.1, 162.6, 147.3, 143.0, 137.3, 133.7, 130.5, 129.0, 125.6, 122.7, 122.4, 120.4, 114.0, 111.1, 54.6, 45.7, 41.0, 33.9, 32.2, 30.5, 29.47, 29.43, 29.40, 29.37, 29.33, 29.0, 28.7, 28.4, 26.9. HRMS (TOF MS ES$^+$) calcd for $C_{62}H_{76}N_4O_6S_2Na$ 1059.5104; found 1059.5125.

***N*-(1,21-Dimercaptoheneicos-11-yl)-*N*′-([1-pyrenyl]methyl)-perylene-3,4,9,10-bis(dicarboximide) (1f). 1-NH$_2$** (18.50 mg, 0.080 mmol) and **7f** (30.00 mg, 0.040 mmol) gave **1f** (34 mg) in 89% yield as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54−8.49 (m, 3H), 8.39 (d, J = 6.0 Hz, 2H), 8.26 (d, J = 9.0, 2H), 8.18 (d, J = 9.0, 2H), 8.03−7.70 (m, 8H), 5.98 (s, 2H), 5.20 (m, 1H), 2.50−2.43 (q, J = 6.0 Hz, 4H), 2.33−2.25 (m, 2H), 1.93−1.88 (m, 2H), 1.56−1.48 (m, 4H), 1.31−1.18 (m, 30H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 134.2, 133.7, 131.3, 130.9, 130.49, 130.44, 130.0, 129.1, 128.9, 128.6, 127.6, 127.0, 125.8, 125.6, 125.0, 124.9, 124.58, 124.54, 124.3, 123.0, 122.8, 122.5, 54.7, 41.3, 33.9, 32.3, 29.55, 29.50, 29.47, 29.40, 28.9, 28.3, 27.0, 24.6. HRMS (TOF MS ES$^+$) calcd for $C_{62}H_{62}N_2O_4S_2Na$ 985.4048; found 985.4070.

***N*-(1,21-Dimercaptoheneicos-11-yl)-*N*′-(2-ferrocenylethyl)-perylene-3,4,9,10-bis(dicarboximide) (3f). 3-NH$_2$** (18.30 mg, 0.080 mmol) and **7f** (30.0 mg, 0.04 mg) gave **3f** (33 mg) in 87% yield as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69−8.60 (m, 8H), 5.20 (m, 1H), 4.43−4.38 (m, 2H), 4.24−4.21 (m, 7H), 4.11 (s, 2H), 2.79 (t, J = 9.0 Hz, 2H), 2.52−2.44 (q, J = 6.0 Hz, 4H), 2.33−2.20 (m, 2H), 1.93−1.83 (m, 2H), 1.58−1.51 (m, 4H + H_2O), 1.32−1.22 (m, 30H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 134.7, 134.3, 131.8, 131.4, 131.1, 129.5, 129.4, 126.5, 126.3, 123.1, 123.0, 85.0, 69.1, 68.6, 68.3, 68.1, 67.5, 54.7, 41.2, 34.0, 32.3, 29.5, 29.46, 29.42, 29.0, 28.3, 27.8, 26.9, 24.6, 24.4. HRMS (TOF MS ES$^+$) calcd for $C_{57}H_{64}FeN_2O_4S_2Na$ 983.3556; found 983.3584.

***N*-(1,21-Bis(methyldisulfanyl)heneicos-11-yl)-*N*′-4-[1-pyrenylmethyl])perylene-3,4,9,10-bis(dicarboximide) (1g). 1-NH$_2$** (21.97 mg, 0.095 mmol) and **7g** (40.00 mg, 0.047 mmol) gave **1g** (41 mg) in 82% yield as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.65−8.55 (m, 5H), 8.47−8.40 (m, 4H), 8.16−7.85 (m 8H), 6.09 (s, 2H), 5.20 (m, 1H), 2.65 (t, J = 6.0 Hz, 4H), 2.38 (s, 6H), 2.36−2.25 (m, 2H), 1.89 (m, 2H), 1.67−1.56 (m, 4H), 1.37−1.20 (m, 28H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 163.2, 133.9, 133.5, 131.0, 130.8, 130.36, 130.33, 130.0, 128.9, 128.6, 128.5, 127.5, 126.9, 125.8, 125.58, 125.51, 125.4, 124.9, 124.8, 124.5, 124.3, 124.2, 122.9, 122.6, 122.3, 54.7, 41.2, 38.3, 32.4, 29.57, 29.51, 29.48, 29.42, 29.3, 29.1, 28.4, 27.0, 23.3. HRMS (TOF MS ES$^+$) calcd for $C_{64}H_{66}N_2O_4S_4Na$ 1077.3803; found 1077.3827.

***N*-(1,21-Bis(methyldisulfanyl)heneicos-11-yl)-*N*′-(2-ferrocenylethyl)perylene-3,4,9,10-bis(dicarboximide) (3g). 3-NH$_2$** (21.76 mg, 0.095 mmol) and **7g** (40.0 mg, 0.047 mmol) gave **3g** (39 mg) in 79% yield as a waxy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64−8.46 (m, 8H), 5.24−5.19 (m, 1H), 4.40 (t, J = 9.0 Hz, 2H), 4.30−4.21 (m, 7H), 4.12 (m, 2H), 2.79 (t, J = 9.0 Hz, 2H), 2.67 (t, J = 6.0 Hz, 4H), 2.41 (s, 6H), 2.30−2.26 (m, 2H), 1.94−1.87 (m, 2H),

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1.67−1.60 (m, 4H), 1.37−1.25 (m, 28H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 163.0, 134.4, 134.1, 131.7, 131.1, 130.9, 129.4, 129.1, 126.2, 126.1, 123.0, 122.98, 122.91, 85.1, 73.1, 69.6, 68.6, 68.1, 67.4, 54.8, 41.2, 38.3, 32.3, 29.5, 29.48, 29.42, 29.1, 28.4, 27.7, 26.9, 23.3. HRMS (TOF MS ES$^+$) calcd for $C_{59}H_{68}FeN_2O_4S_4Na$ 1075.3311; found 1075.3282.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for new compounds. 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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■ NOTE ADDED AFTER ASAP PUBLICATION

After ASAP publication on October 22, 2012, corrections were made to the experimental data for compounds **10**, **6b**, and **3b** in the Experimental Section; the correct version reposted October 23, 2012.