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Synthesis of Emissive Heteroacene Derivatives via Nucleophilic Aromatic Substitution

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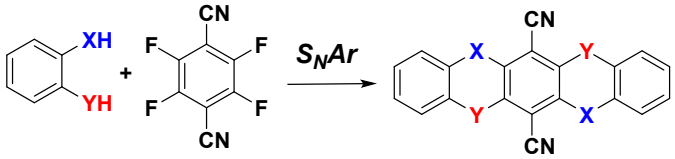
Supporting Information Placeholder



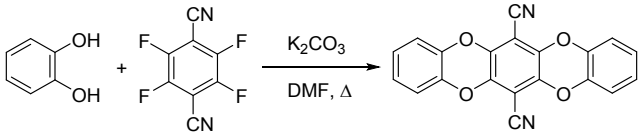
ABSTRACT: A synthetic approach for preparing a variety of heterocyclic tetrahydropentacene derivatives via nucleophilic aromatic substitution reactions of bidentate nucleophiles and tetrafluoroterephthalonitrile was developed. X-ray crystallography of several products revealed that the compounds containing oxygen and nitrogen heteroatoms are highly planar and engage in π-stacking, while the compounds containing sulfur are bent and they do not stack as effectively. The compounds were also highly emissive and the heteroatom had a significant impact on the emission and electrochemical properties.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are the focus of intense research interest. This is in part because of their π-conjugated structures that make them suitable for use in organic electronics and as dyes.[1–5] More recently, attention has focused on heteroaromatic PAHs because the heteroatom substitution can influence the electronic properties, stability, and solid state packing, which collectively in turn, impact the overall device performance.[6–8]

Dicyanotetraoxapentacene (DCTOP, **1**) is a planar, pentacyclic compound that resembles a heteropentacene. It is readily prepared by nucleophilic aromatic substitution using catechol and tetrafluoroterephthalonitrile (TFN) (Scheme 1). This motif has been used for the preparation of rigid, macromolecular networks such as polymers with intrinsic microporosity,[9–13] covalent organic frameworks,[14,15] as well as cyclodextrin-based polymers for wastewater treatment.[16,17] In these examples, the DCTOP moiety serves primarily as a rigid linker. Recently, we showed that dialkoxyphenyl DCTOP derivatives exhibit columnar mesophases and they have aggregation-induced emission.[18] Given the interesting properties of these materials, their similarity to heteroacenes, and their potential as luminescent dyes, there is an interest in exploring this synthetic approach for the preparation of other heteroacene analogs.

Scheme 1. Synthesis of Compound 1.



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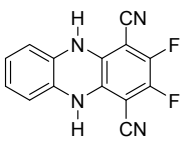
The nucleophilic aromatic substitution approach using tetrafluoroterephthalonitrile could be extended to a variety of tetrahydroheteropentacene systems. However, the reaction scope of bidentate nucleophiles with TFN has received little attention. In one example, TFN was reacted with a number of bidentate arene nucleophiles derivatives using ultrasound conditions.[19] Analogs in which the oxygen atoms of the nucleophile are replaced with N or S were reported, including dihydrophenazine (**2**) and thianthrene (**3**).



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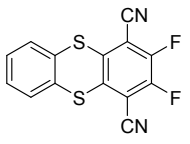


3

However, these reactions have not been extended to the corresponding heteropentacene analogs. In another example,

Swager and coworkers reported that dithiophenol reacts with TFN and related polyfluorinated benzene derivatives and they demonstrated that this nucleophilic aromatic substitution reaction can be reversible.[20] Further, nucleophilic aromatic substitution on brominated naphthalene diimides and related imides with a variety of bidentate aromatic nucleophiles has been successfully used to prepare extended imide-functionalized heteroacene derivatives, suggesting the that this approach could be used to access other types of heteroacenes.[21–23]

In this study, we report nucleophilic aromatic substitution reactions with TFN and a variety of bidentate nucleophiles to prepare several novel heterocyclic tetrahydropentacene derivatives that behave as luminescent dyes (Figure 1, compounds **1**, **4-7**). We also demonstrate that the heteroatom substitution in these systems has a dramatic impact on the solid-state structures, the emission, and the electrochemical properties of these materials.

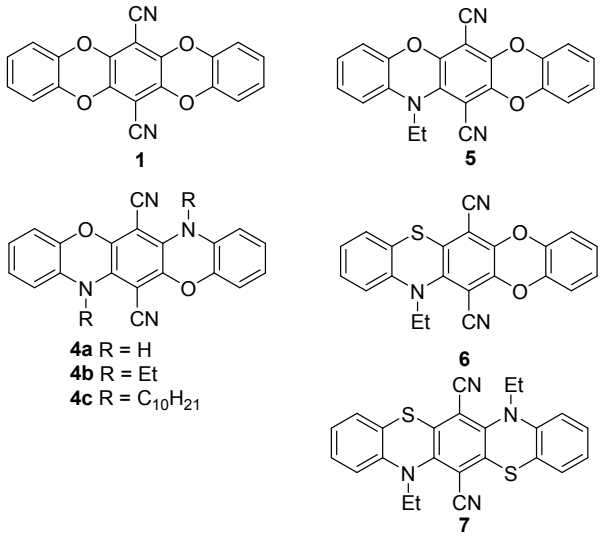
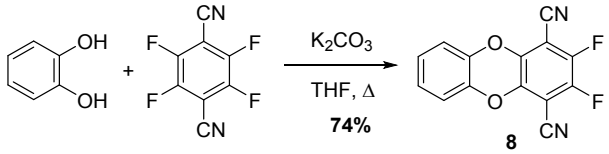


Figure 1. Target compounds in this study.

RESULTS AND DISCUSSION

Compound **1** was prepared as according to literature procedures by reacting catechol with TFN in DMF in the presence of K_2CO_3.[24] It is noteworthy that the preparation of the corresponding dibenzodioxin (**8**), where only one equivalent of catechol reacts with TFN, can be prepared under similar conditions with THF as the solvent (Scheme 2).

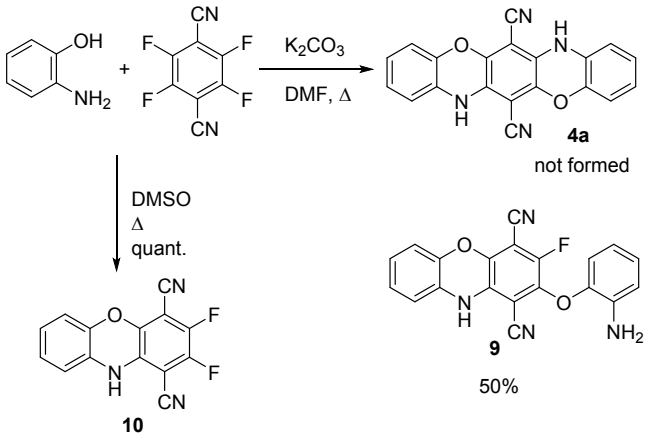
Scheme 2. Synthesis of dibenzodioxin 8.



For our initial attempts to prepare the corresponding diazadioxapentacene analog (compound **4a**), we employed the same reaction conditions using commercially available 2-aminophenol. Unfortunately, the desired product was not isolated. The reaction mixture turned a dark purple and a red solid was obtained upon workup. The red solid was a mixture of products where the major component was compound **9** (Scheme 3), which was isolated in 50% yield. In compound **9**, one equivalent of 2-aminophenol reacts as expected, but the second equivalent does not undergo the final cyclization by nucleophilic aromatic substitution (Scheme 3). The structure of **9** was confirmed by X-ray crystallography (see Supporting Information).

The dark purple colour of the reaction mixture was attributed to deprotonation of the cyclized phenoxazine intermediate, which likely deactivates the para position to nucleophilic substitution, explaining why full cyclization to form **4a** was unsuccessful. To test this hypothesis, the reaction was conducted in the absence of base in DMSO. Under these conditions, difluorophenoxazine **10** was formed in quantitative yield. However, the desired compound **4a** was not observed.

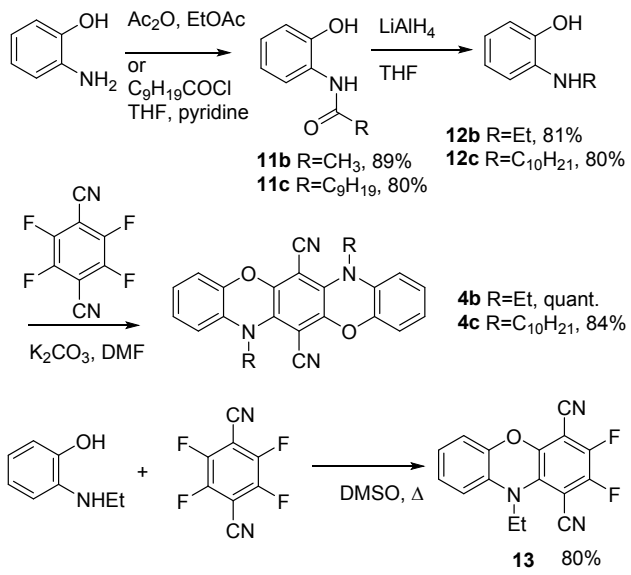
Scheme 3. Attempted Synthesis of 4a.



To circumvent the deactivation that results from the amide ion of **10** under basic conditions, we sought to test the reactivity of corresponding *N*-alkyl amino phenols **12b** and **12c**. Compounds **12b** and **12c** were prepared via acetylation, followed by reduction using $LiAlH_4$ (Scheme 4). Gratifyingly, the reaction of **12b** and **12c** with TFN in the presence of K_2CO_3 in DMF gave the targeted pentacyclic systems **4b** and **4c** as red, crystalline solids in good yields. Furthermore, reacting **12b** with TFN in DMSO in the absence of base furnished the corresponding *N*-ethylphenoxazine (**13**) in 80% yield.

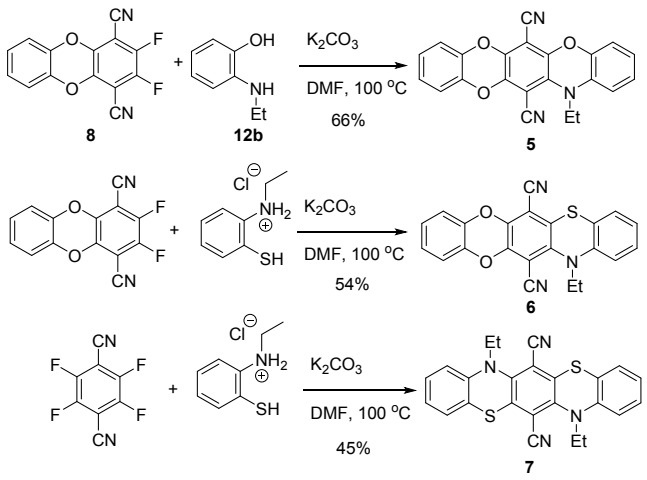
The preparation of dibenzodioxin **8** and *N*-ethylphenoxazine **13** demonstrate that the reaction with TFN can be controlled so that nucleophilic aromatic substitution to produce cyclic products only occurs on one side of the molecule. This result is consistent with the notion that the first two nucleophilic aromatic substitution reactions occur readily and the product of this reaction is less activated towards further substitution because of the electron-donating heteroatoms. However, by altering the reaction conditions, these compounds can react further, opening up the possibility of producing a variety of compounds with varied heteroatom substitution patterns. To demonstrate that sequential nucleophilic aromatic substitution reactions can be used to produce dissymmetric heteropentacene analogs, dibenzodioxin **8** was reacted with *N*-ethyl-2aminophenol to furnish compound **5** in 66% yield (Scheme 5).

Scheme 4. Synthesis of compounds 4b-c and 13.



Finally, we explored the introduction of sulfur atoms into these heterocyclic systems, given that thiolates are highly nucleophilic. To this end, *N*-ethyl-2-aminothiophenol was prepared by reduction of 2-methyl benzothiazole[25] and reacted with tetrafluoroterephthalonitrile and dibenzodioxin **8** to furnish compounds **6** and **7** in moderate yields (Scheme 5). In contrast to **4b,c** the analogous reaction to form **7** produced two major products (TLC) of very similar R_f which proved inseparable by column chromatography. Crystallisation of the mixture from THF yielded compound **7**, confirmed by X-ray crystallography, while the second component, thought to be the corresponding *syn* isomer, eludes full purification.

Scheme 5. Synthesis of compounds 5-7.



In order to gain insight into the molecular geometry of these compounds and explore their solid state packing, crystals of compounds **1**, **4c**, **6**, and **7** were grown and they were studied by single crystal X-ray diffraction. Compound **1** is known, and the crystal structure was recently reported from crystals grown from acetonitrile.[14] In our hands, crystals of **1** that were suitable for X-ray diffraction were grown by the slow evaporation of a solution in mesitylene, yielding a crystal structure that agreed with the previously reported structure. The polycyclic compound is highly planar with a root mean squared deviation from planarity of 0.039 Å. Each molecule engages in π-stacking interactions with four neighbouring molecules; two molecules each above and below the plane of the aromatic system (See Supporting Information.)

We were unsuccessful in growing crystals of ethyl-substituted **4b** that were suitable for X-ray diffraction. However, we were able to grow crystals of the corresponding decyl-substituted derivative (**4c**) by the slow diffusion of acetonitrile into a saturated chlorobenzene solution. Compound **4c** crystallized in a triclinic space group (P-1) with one molecule per unit cell. Similar to **1**, the polycyclic core of **4c** was highly planar with a root mean squared deviation from planarity of 0.099 Å (Figure 2). The packing of **4c** shows stacking where the central ring interacts with the terminal ring of an adjacent molecule at a distance of 3.84 Å and shift of 1.37 Å (See Supporting Information).

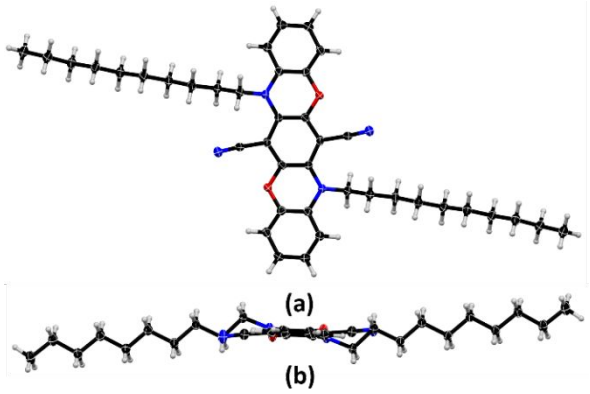


Figure 2. Crystal structure of compound **4c** with 50% displacement ellipsoids. Views (a) and (b) rotated by 90°.

Crystals of **6** were grown from ethyl acetate via the slow evaporation. Unlike the highly planar compounds **1** and **4c**, the introduction of a sulfur atom leads to a bent structure (Figure 3). It nonetheless still engages in π-stacking interactions with centroid distances of 3.60 and 3.63 Å with respect to the terminal dibenzodioxin and central dicyanobenzene rings.

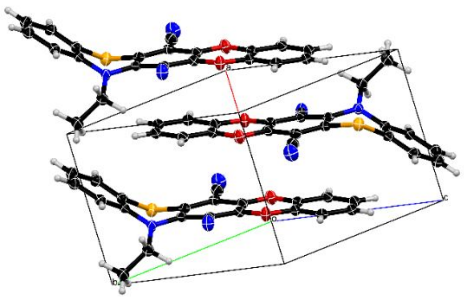


Figure 3. Crystal structure of compound **6** with 50% displacement ellipsoids.

Crystals of compound **7** were grown from the slow evaporation of a solution in THF. Similar to compound **6**, the sulfur-containing rings adopt a nonplanar geometry with a fold angle of 40.06(8)° (Figure 4). However, in contrast to compounds **1**, **4c**, and **6**, there are no discernible π-stacking interactions in the solid state. This is possibly because the bent structure impedes the close approach of neighboring aromatic rings.

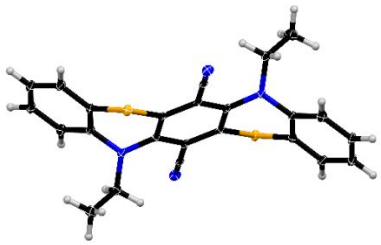


Figure 4. Crystal structure of **7** with 50% displacement ellipsoids.

The colours of the compounds prepared in this series range from yellow to orange-red and they are highly emissive in solution. We therefore investigated their emission in both solution and the solid state. The collective absorption and emission spectra are shown in Figure 5 with emission data summarized in Table 1.

Table 1. Emission data of the Tetrahydroheteroacenes in chloroform.

	1	**4b**	**5**	**6**	**7**
Φ[a] (excitation λ, nm)[b]	78% (430)	44% (495)	34% (470)	23% (465)	32% (495)
Abs. (nm)[c]	430	495	470	460	495
Em. (nm)[d]	475	615	555	580	615
[e]	390	470	450	450	470

[a] Measured with a calibrated integrating sphere. [b] Value in parentheses is the excitation wavelength used for measuring the quantum yields. [c] Absorption maximum. [d] Emission maximum. [e] Excitation wavelength for measuring the emission spectrum.

The fluorescence quantum yields in chloroform range from 23% to 78%, confirming that these compounds are all emissive in solution. Owing to the compounds' small Stokes shift in solution, exciting at their absorption maximum would truncate the emission spectrum. This would result in erroneously low emission yields. Excitation wavelengths shorter than the corresponding absorption maximum of the compounds were therefore used for measuring the Φ_{fl} in solution. These were done to ensure that the full emission spectrum was measured. Accurate Φ_{fl} are expected with this approach, especially since the emission yield is independent of the excitation wavelength.

In contrast, the fluorescence quantum yields of thin films are significantly lower (see Supporting Information). This is consistent with conventional aggregation caused quenching. From the absorption and emission spectra, two patterns are apparent. First, substitution of oxygen atoms for nitrogen atoms leads to a red shift in both the absorption and emission spectra. For example, compound **1** shows an emission maximum of 478 nm, compound **5** (bearing one nitrogen) has an emission maximum of 556 nm, and compound **4b** (bearing two nitrogen atoms) has an emission maximum of 615 nm. Interestingly, replacement of oxygen atoms by sulfur atoms has only very slight influence on the absorption and emission spectra, i.e. **4b** vs. **7** and **5** vs. **6**. However, the quantum yield of fluorescence decreases when sulfur atoms are introduced. This is expected owing to increased spin orbit coupling with the heavier atom, resulting in increased deactivation of the singlet excited state by intersystem crossing.

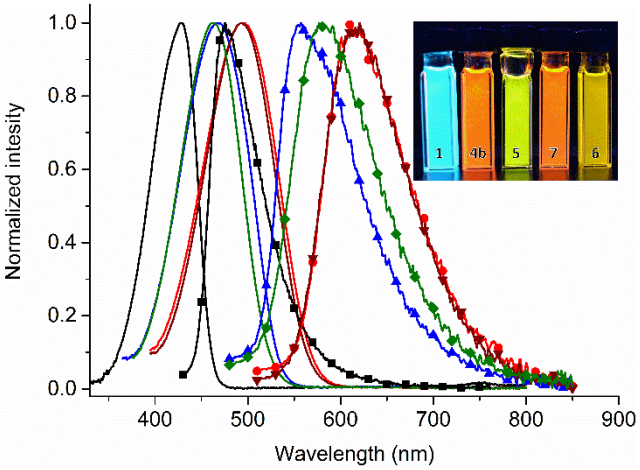


Figure 5. Normalized absorption (solid line) emission (symbol) spectra for **1** (—, ■), **4b** (—, •), **5** (—, ▲), **6** (—, ♦), and **7** (—, ▼) measured in chloroform. Inset: solutions in chloroform irradiated with a hand-held UV lamp.

The redox properties of the compounds were investigated by both cyclic voltammetry and square wave voltammetry in dichloromethane (see Supporting Information). Compound **1** showed no clear oxidation wave over the potential range scanned, while compound **5** showed a quasi-reversible two-electron oxidation peak at 595 mV vs. ferrocene. In contrast, compounds **4b** and **7** each showed two reversible oxidation peaks with oxidation potentials of 265 and 780 mV for **4b** and 515 and 835 mV for **7**. Compound **6** showed a single one-electron quasi-reversible oxidation at 725 mV. The non-reversible oxidation behavior of **6** and **7** is further supported by electrochemically produced products that were observed in the reverse wave of the anodic voltammogram. Overall, the observed order of the oxidation potentials is consistent with the calculated HOMO energies (see Supporting Information).

CONCLUSIONS

In summary, we report a synthetic approach to heterocyclic tetrahydropentacene derivatives via nucleophilic aromatic

substitution using tetrafluoroterephthalonitrile. Using this approach, we were able to access several different heterocyclic compounds containing O, N, and S. X-ray crystallography reveals that the N and O-containing compounds (**1** and **4**) were highly planar and they exhibited some π-stacking in the solid state. Meanwhile, the sulfur containing compounds **6** and **7** were bent and they exhibited less π-stacking. All the compounds were highly emissive in solution with the heteroatom substitution significantly affecting the absorption and emission in addition to the absolute quantum yields. While all the compounds were electroactive, they could only be oxidized. Similar to the spectroscopic properties, the oxidation potential and the electrochemical reversibility of tetrahydropentacene derivatives were also contingent on their heteroatom.

EXPERIMENTAL

Synthetic Procedures

General

^{1}H and ^{13}C spectra were recorded on an Agilent Technologies Varian 300 MHz Unity Inova NMR Spectrometer or 400 MHz NMR Spectrometer using the indicated deuterated solvents purchased from Sigma-Aldrich. Chemical shifts are reported in δ scale downfield from the peak for tetramethylsilane. High resolution mass spectra were recorded at the Centre Régional de Spectrométrie de Masse à l'Université de Montréal using an Agilent LC-MSD TOF spectrometer. All reagents and starting materials were purchased from Sigma-Aldrich and used as purchased. Anhydrous solvents were dispensed using a custom-built solvent system from Glasscontour (Irvine, CA) which used purification columns packed with activated alumina and supported copper catalyst. Oven-dried glassware was used for all reactions that were performed under nitrogen. Melting points were determined on a Mel-Temp® Electrothermal melting point apparatus and are uncorrected.

***N*-(2-hydroxyphenyl)acetamide (11b):** To a 500 mL round bottomed flask was added 2-aminophenol (5.00 g, 45.8 mmol, 1.0 eq), EtOAc (100 mL), followed by acetic anhydride (4.70 mL, 50.4 mmol, 1.1 eq). This was stirred at room temperature for 4 h, diethyl ether (100 mL) was added and the mixture cooled to ~5 °C. The precipitate was collected as a grey powder *via* suction filtration, washing with diethyl ether. The crude product was recrystallized from aqueous ethanol as off-white plates (6.11 g, 89%). mp (EtOH/H_2O) = 208-209 °C (lit. mp = 209 °C); ^{1}H NMR (400 MHz, CD_3OD) *δ*:7.57 (d, *J* = 7.6 Hz, 1H), 7.01-6.98 (m, 1H), 6.86-6.78 (m 2H), 2.17 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD) *δ*: 172.2, 149.7, 127.1, 126.8, 123.9, 120.6, 117.3, 23.4. Analytical data agrees with literature values.[26]

2-(*N*-ethylamino)phenol (12b): To a dry, 250 mL three-neck round bottomed flask, equipped with a dried stir bar, condenser, and N_2 inlet, was added *N*-(2-hydroxyphenyl)acetamide **11b** (1.50 g, 9.92 mmol, 1.0 eq) and THF (75 mL). This was then cooled to 0 °C, and lithium aluminum hydride (1.0 M in THF, 19.8 mL, 2.0 eq) was added dropwise, pausing as appropriate for hydrogen evolution. The ice bath was then replaced with an oil bath and the reaction mixture heated to reflux. After 12 h, the reaction was cooled to 0 °C and sodium sulfate decahydrate ($Na_2SO_4 \cdot 10H_2O$) was added in *small* portions, over approximately 25 min, until hydrogen evolution subsided. Aqueous ammonium chloride was then added until neutral, and the emulsion thus obtained filtered through a pad of Celite®, washing the filter cake with diethyl ether. The volatiles were then removed *in vacuo*, the residue partitioned between ether and H_2O, and the aqueous layer extracted with ether (3 x 20 mL). The pooled organic extracts were washed with saturated aqueous $NaHCO_3$ (20 mL), brine (20 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was recrystallized from chloroform (−20 °C) to give the product as white needles (1.10 g, 81%), stored at −20 °C to slow decomposition. mp ($CHCl_3$) = 105 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 6.87-6.83 (m, 1H), 6.70-6.60 (m, 3H), 4.12 (br s, 2H), 3.15 (q, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) *δ*: 143.7, 137.1, 121.6, 117.8, 114.3, 112.7, 38.9, 14.8. Analytical data agrees with literature values.[27]

***N*-(2-hydroxyphenyl)decanamide (11c):** To a 250 mL round bottomed flask was added 2-aminophenol (2.50 g, 22.9 mmol, 1.0 eq), THF (100 mL), pyridine (4.1 mL, 50 mmol, 2.2 eq). This was stirred until dissolution, and decanoyl chloride (4.8 mL, 23 mmol, 1.0 eq) was added dropwise causing a precipitate which dissolved by the end of addition. This was left to stir under N_2 overnight (18 h). Volatiles were removed *in vacuo*, and the residue was partitioned between chloroform and water. The aqueous layer was extracted with chloroform (2 x 25 mL) and the pooled organic solvents washed with 1 M HCl (25 mL), H_2O (25 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude solid thus obtained was recrystallized from aqueous methanol to yield *N*-(2-hydroxyphenyl)decanamide as a white fluffy solid (4.39 g, 73%). mp (MeOH/H_2O) = 67-68 °C (lit. 71 °C);[28] ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.96 (s, 1H), 7.92 (s, 1H), 7.14-7.06 (m, 2H), 6.97 (d, *J* = 7.8 Hz, 1H), 6.84 (t, *J* = 7.6 Hz, 1H), 2.42 (t, *J* = 7.5 Hz, 2H), 1.75-1.68 (m, 2H), 1.35-1.24 (m, 14H), 0.87 (t, *J* = 6.7 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) *δ*: 173.7, 148.6, 127.0, 125.6, 122.0, 120.3, 119.7, 37.0, 31.8, 29.4, 29.3, 29.2, 29.1, 25.7, 22.6, 14.0.

2-(*N*-decylamino)phenol (12c): To a 250 mL two-neck round-bottomed flask, equipped with a reflux condenser under N_2 and equipped with an addition funnel, was added lithium aluminum hydride (0.915 g, 24.1 mmol, 2.0 eq) and THF (60 mL), and this was cooled to 0 °C. A solution of *N*-(2-hydroxyphenyl)decanamide **11c** (3.17 g, 12.0 mmol, 1.0 eq) in THF (35 mL) was then added dropwise *via* addition funnel to the cold reaction flask over 15 minutes. The ice bath was then replaced with an oil bath and the mixture gradually brought to reflux for 12 h, after which time the mixture was cooled to 0 °C and quenched *via* cautious addition of $Na_2SO_4 \bullet 10H_2O$ in small portions. The mixture was then brought to neutral pH with saturated NH_4Cl (pH paper), filtered through Celite®, and concentrated *in vacuo*. The residue was dissolved in EtOAc (50 mL), washed with saturated $NaHCO_3$ (20 mL), H_2O (20 mL), and brine (40 ml). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo* to give the aminophenol as a purple solid, which was used for the following reactions

without further purification (2.40 g, 80%). mp (hexanes) = 65 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.90-6.84 (m, 1H), 6.72-6.62 (m, 3H), 4.46 (br s, 2H), 3.13-3.10 (m, 2H), 1.68-1.61 (m, 2H), 1.45-1.29 (m, 14H), 0.90 (t, J = 6.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 143.7, 137.2, 121.5, 117.6, 114.3, 112.5, 44.5, 31.9, 29.6, 29.5, 29.4, 29.3, 27.2, 22.6, 14.1.

7,14-diethyl-7,14-dihydrobenzo[5,6][1,4]oxazino[2,3-b]phenoxazine-6,13-dicarbonitrile (4b): To a 25 mL round bottomed flask, under N_2, was added 2-(*N*-ethylamino)phenol **12b** (120 mg, 0.875 mmol, 2.0 eq), tetrafluoroterephthalonitrile (88 mg, 0.44 mmol, 1.0 eq), DMF (5 mL), and finally K_2CO_3 (726 mg, 5.25 mmol, 6.0 eq). This was stirred and heated to 100 °C for 24 h in an oil bath, after which time the mixture was cooled to rt and poured into H_2O (75 mL). After cooling overnight, the precipitate was collected as a red solid which was recrystallized from chloroform-methanol (172 mg, 100%). mp > 260 °C; R_f(50% EtOAc/Hexanes) = 0.33; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.03-6.84 (m, 8H), 3.94 (t, J = 7.0 Hz, 4H), 1.28 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 148.0, 147.5, 132.7, 131.5, 125.3, 124.4, 118.9, 116.5, 112.9, 95.0, 48.7, 13.2; HRMS (ESI) m/z: $[M+H]^+$ Calc. for $C_{24}H_{19}N_4O_2$ 395.1503; Found 395.1505.

7,14-didecyl-7,14-dihydrobenzo[5,6][1,4]oxazino[2,3-b]phenoxazine-6,13-dicarbonitrile (4c): To a 50 mL round-bottomed flask was added tetrafluoroterephthalonitrile (225 mg, 1.12 mmol, 1.0 eq), K_2CO_3 (1.24 g, 8.96 mmol, 8.0 eq), and DMF (20 mL). This was placed under N_2 and **12c** (560 mg, 2.25 mmol, 2.0 eq) was added in portions. The mixture was heated to 100 °C in an oil bath. After 24 h, the mixture was cooled, poured into H_2O (125 mL), and the red solid collected *via* suction filtration, washing with H_2O. This was then recrystallised from toluene-methanol to yield the product as a red, microcrystalline solid (583 mg, 84%). mp = 145-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.03-6.99 (m, 2H), 6.94-6.89 (m, 4H), 6.83 (d, J = 7.9 Hz, 2H), 3.88 (t, J = 7.5 Hz, 4H), 1.70-1.62 (m, 4H), 1.33-1.21 (m, 28H), 0.86 (t, J = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 147.7, 147.4, 133.1, 131.8, 125.2, 124.1, 118.6, 116.4, 112.9, 94.7, 53.1, 31.8, 29.47, 29.45, 29.2, 29.1, 27.4, 26.2, 22.6, 14.1.

2,3-difluoro-10H-phenoxazine-1,4-dicarbonitrile (10): To a 250 mL round-bottomed flask was added 2-aminophenol (1.43 g, 13.1 mmol, 1.0 eq), tetrafluoroterephthalonitrile (2.62 g, 13.1 mmol, 1.0 eq), and DMSO (65 mL). This was equipped with a drying tube ($CaSO_4$) and stirred at rt for 18 h, by which time a bright orange solid had precipitated. H_2O (200 mL) was added to effect full precipitation and the product was collected *via* suction filtration (3.50 g, 100%). This powdery solid could be recrystallised from hot DMF to afford long orange needles. mp (DMF) > 260 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.58 (s, 1H), 6.90 (s, 2H), 6.81 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, acetone-d_6) δ: 145.8 (dd, J_{C-F} = 250.1, 13.6 Hz), 144.6, 142.4 (dd, J_{C-F} = 248.1, 14.7 Hz), 142.3, 135.4, 128.8, 126.8, 124.8, 116.7, 116.3, 110.5 (d, J_{C-F} = 3.4 Hz), 109.5 (d, J_{C-F} = 3.5 Hz), 95.6 (d, J_{C-F} = 15.8 Hz), 89.7 (d, J_{C-F} = 18.9 Hz); ^{19}F NMR (282 MHz, acetone-d_6) δ: −142.3 (d, J = 20 Hz), −148.16 (d, J = 20 Hz); IR (ATR) ν_{max}: 3157 (w), 3113 (w), 3063 (w), 2951, 2898, 2239, 2230, 1470, 1288, 1023, 993, 759 cm^{-1}; HRMS (APCI) m/z: $[M]^+$ Calc. for $C_{14}H_5N_3OF_2$ 269.0401; Found 269.0391.

10-ethyl-2,3-difluoro-10H-phenoxazine-1,4-dicarbonitrile (13): To a 25 mL pear-shaped flask was added tetrafluoroterephthalonitrile (559 mg, 2.79 mmol, 1.0 eq), followed by DMSO. This was warmed to dissolution (50 °C) and 2-(ethylamino)phenol **12b** (383 mg, 2.79 mmol, 1.0 eq) was added in portions. This was stirred at room temperature for 24 h, after which time H_2O (60 mL) was added and the solid collected *via* suction filtration, washing with water. The powder thus obtained was recrystallised from acetonitrile to furnish the product as long, orange needles (665 mg, 80%). mp (MeCN) = 223-225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.05 (t, J = 7.6 Hz, 1H), 6.96 (t, J = 7.6 Hz, 1H), 6.91-6.89 (m, 1H), 6.85-6.83 (m, 1H), 4.04 (q, J = 6.9 Hz, 2H), 1.38 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 147.8 (t, J_{C-F} = 3.3 Hz), 146.4 (dd, J_{C-F} = 255.0, 13.5 Hz), 145.5, 143.0 (dd, J_{C-F} = 255.8, 14.9 Hz), 135.8 (dd, J_{C-F} = 3.3, 1.4 Hz), 131.0, 126.1, 125.0, 117.0, 116.6, 111.2 (d, J_{C-F} = 3.6 Hz), 108.7 (d, J_{C-F} = 3.9 Hz), 95.7 (dd, J_{C-F} = 16.6, 3.0 Hz), 93.5 (d, J_{C-F} = 17.1 Hz), 46.6, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ: -135.4 (d, J = 21 Hz), -140.5 (d, J = 21 Hz); HRMS (ESI) m/z: $[M+H]^+$ Calc. for $C_{16}H_{10}F_2N_3O$ 298.0786; Found 298.0791.

2-(2-aminophenoxy)-3-fluoro-10H-phenoxazine-1,4-dicarbonitrile (9): To a 50 mL round-bottomed flask, under N_2, was added tetrafluoroterephthalonitrile (600 mg, 3.00 mmol, 1.0 eq), 2-aminophenol (654 mg, 6.00 mmol, 2.0 eq), dry DMF (20 mL), and finally K_2CO_3 (3.32 g, 24.0 mmol, 8.0 eq). The mixture was heated to 65 °C in an oil bath and quickly became a deep purple colour; this was left to stir 20 h. The reaction mixture was cooled to rt, then H_2O was then added effecting precipitation of a reddish-brown solid, collected *via* suction filtration, and triturated with acetonitrile yielding a mixture of products (400 mg) from which a single crystal (DMF) subjected to X-ray diffraction identified that component as the title compound. IR(ATR) ν_{max} = 3445, 3360, 3279, 2250, 2236, 1626, 1570, 1499, 1466, 1383, 1287, 1196, 1173, 1033, 996, 749, 731 cm^{-1}; HRMS (ESI) m/z: $[M+H]^+$ Calc. for $C_{20}H_{12}FN_4O_2$ 359.0939; Found 359.0949.

2,3-difluorodibenzo[b,e][1,4]dioxine-1,4-dicarbonitrile (8): To a 250 mL single neck round-bottomed flask was added catechol (2.00 g, 18.2 mmol, 1 eq), tetrafluoroterephthalonitrile (3.64 g, 18.2 mmol, 1 eq), and potassium carbonate (7.53 g, 54.5 mmol, 3 eq) followed by dry THF (150 mL). The flask was equipped with a condenser under N_2 and the mixture was heated in an oil bath at reflux with stirring for 2 h, then stirred at rt for 8 h. After this time H_2O (150 mL) was added to effect crystallization of the product and the mixture was cooled to ~5 °C. The yellow suspension was suction filtered, washed three times with H_2O and dried to give the product as a yellow powdery solid which was recrystallised from DME to give the product as very light-yellow plates (3.62 g, 74%). mp (DME) = 209-210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.09-7.02 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ: 145.7 (dd, J_{C-F} = 261.4, 15.8 Hz), 141.4 (t, J = 3.5 Hz), 139.3, 126.4, 117.1, 107.7 (d, J_{C-F} = 1.9 Hz), 96.7 (dd, J_{C-F} = 11.2, 7.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: -134.7. Analytical data agrees with literature values.[29]

14-ethyl-14H-benzo[5,6][1,4]dioxino[2,3-b]phenoxazine-6,13-dicarbonitrile (5): To a 50 mL round-bottomed flask was added difluoride **8** (905 mg, 3.35 mmol, 1.0 eq) and DMF (15 mL) under N_2. K_2CO_3 (1.85 g, 13.4 mmol, 4.0 eq) was then added, followed by 2-(*N*-ethylamino)phenol **12b** (459 mg, 3.35 mmol, 1.0 eq). This was heated to 100 °C for 24 h in an oil bath, after which time the orange mixture was cooled, poured into H_2O, and then filtered. The collected precipitate was recrystallised from toluene-methanol to yield the title compound as an orange crystalline solid (851 mg, 70%). mp (PhMe/MeOH) = 241 °C (dec.); R_f = 0.38 (50% $CHCl_3$/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.04-6.84 (m, 8H), 3.96 (q, J = 6.9 Hz, 2H), 1.29 (t, J = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 146.9, 146.7, 140.1, 140.0, 139.6, 137.1, 133.6, 132.0, 125.8, 125.49, 125.46, 124.5, 118.4, 1170, 116.9, 116.8, 116.3, 112.1, 109.9, 48.2, 13.1; HRMS (ESI) m/z: [M+H] Calc. for $C_{22}H_{14}N_3O_3$ 368.1030; Found 368.1037.

2-(*N*-ethylamino)thiophenol hydrochloride (14): To a dry 250 mL three-neck round-bottomed flask equipped with a reflux condenser was added dry THF (75 mL), solid lithium aluminum hydride (2.54 g, 66.8 mmol, 1.0 eq), and this was cooled to 0 °C (ice bath) under N_2. To the stirred suspension was added a solution of 2-methylbenzothiazole (9.97 g, 66.8 mmol, 1.0 eq) in dry THF (10 mL), dropwise. After addition was complete, the ice bath was replaced with an oil bath and the mixture heated to reflux for 3 h. The yellow mixture was cooled to 0 °C and decomposed (carefully) with wet THF (15 mL THF, 5 mL H_2O). The pH was then brought to ≈2-3 (pH paper) with concentrated HCl (9-10 mL) and the mixture filtered through Celite®, washing with Et_2O. The crude solution was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give a yellow viscous oil which was dissolved in ^{i}PrOH and concentrated HCl (5.9 mL) was added dropwise with stirring. Addition of Et_2O just until cloudy, followed by cooling overnight (−15 °C) gave the product as a light yellow crystals, collected by suction filtration, and washing with cold Et_2O (7.10 g, 37.4 mmol, 56%). mp (^{i}PrOH/Et_2O) = 123-124 °C; ^{1}H NMR (400 MHz, D_2O) δ: 7.66 (ddt, J = 4.6, 3.6, 1.2 Hz, 1H), 7.46-7.39 (m, 3H), 3.51 (qd, J = 7.3, 1.4 Hz, 2H), 1.33 (td, J = 7.3, 1.4 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, D_2O) δ: 135.7, 134.4, 130.1, 128.6, 124.9, 123.7, 46.6, 10.1.

12-ethyl-12H-benzo[5,6][1,4]dioxino[2,3-b]phenothiazine-6,13-dicarbonitrile (6): To a 25 mL round-bottomed flask was added dibenzodioxin difluoride **8** (1.42 g, 5.27 mmol, 1.0 eq), K_2CO_3 (2.91 g, 21.08 mmol, 4.0 eq), and dry DMF (24 mL). This was placed under N_2, and a solution of 2-(ethylamino)thiophenol hydrochloride **14** (1.00 g, 5.27 mmol, 1.0 eq) in DMF (15 mL) was added dropwise. The reaction mixture was heated in an oil bath at 100 °C for 36h. Subsequently, the mixture was cooled to room temperature, poured into H_2O (200 mL), and the precipitate collected *via* suction filtration, washing with H_2O. The crude solid thus obtained was recrystallised from EtOAc to yield the product as orange needles (1.10 g, 2.86 mmol, 54%). mp (EtOAc) = 243-244 °C; ^{1}H NMR (400 MHz, C_6D_6) δ: 6.83-6.78 (m, 2H), 6.64 (t, J = 7.5 Hz, 1H), 6.53-6.43 (m, 5H), 3.80 (q, J = 7.0 Hz, 2H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, C_6D_6) δ: 143.3, 143.2, 140.1, 139.8, 139.4, 129.4, 128.0, 127.2, 126.2, 125.2, 125.1, 124.9, 124.5, 120.4, 116.5, 116.4, 112.0, 111.0, 102.9, 97.2, 48.4, 13.9; HRMS (ESI) m/z: $[M+H]^+$ Calc. for $C_{22}H_{14}N_3O_2S$ 384.0801; Found 384.0788.

7,14-diethyl-7,14-dihydrobenzo[5,6][1,4]thiazino[2,3-b]phenothiazine-6,13-dicarbonitrile (7): To a 25 mL two-neck round-bottomed flask, under N_2, was added tetrafluoroterephthalonitrile (158 mg, 0.791 mmol, 1.0 eq), K_2CO_3 (1.66 g, 6.32 mmol, 8.0 eq) and dry DMF (10 mL). A solution of 2-(*N*-ethylamino)thiophenol **14** (300 mg, 1.58 mmol, 2.0 eq) in DMF (5 mL) was then added dropwise. After addition was complete the orange mixture was heated to 100 °C for 12 h in an oil bath, turning dark red in colour. The mixture was cooled, diluted with H_2O (100 mL), and the precipitate collected *via* suction filtration, washing with H_2O, then cold methanol. Recrystallisation of this material from THF provided the desired product as a bright orange solid (150 mg, 0.352 mmol, 45%). mp (THF) > 260 °C; R_f = 0.40 (50% CH_2Cl_2/hexanes); ^{1}H NMR (400 MHz, C_6D_6) δ: 6.83-6.80 (m, 4H), 6.63 (t, J = 7.4 Hz, 2H), 6.51 (d, J = 8.2 Hz, 2H), 3.75 (q, J = 7.0 Hz, 4H), 0.88 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 144.1, 143.6, 136.7, 128.4, 127.4, 126.1, 124.7, 120.8, 114.5, 105.9, 49.3, 14.4; HRMS (ESI) m/z: $[M+H]^+$ Calc. for $C_{24}H_{19}N_4S_2$ 427.1046; Found 427.1047.

X-Ray Crystallography

Data were collected at 110(2) K on a Kappa Nonius CCD diffractometer with Cu *K*α radiation (**1**, **4c** and **6**) or on a Bruker APEX-II CCD diffractometer with Mo *K*α radiation (**7** and **9**.) While data collection and integration for **1**, **4c**, **6** and **9** were straight-forward, crystals of **7** were not of excellent quality and data processing was non-trivial. Multiple integrations were attempted using Rigaku's CrysAlis^{Pro} software, with the data treated as generated from a single crystal, a two-domain twin, a multi-component twin, and a multi-crystal. While all yielded the same unit cell dimensions and contents, the most satisfactory model, wherein all non-hydrogen atoms were treated anisotropically without restraints, was obtained for the integrated data of the multi-crystal second component.

Using Olex2[30], the structures of **1**, **4c**, **6**, **7**, and **9** were solved with the ShelXT[31] structure solution program using intrinsic phasing and refined with the ShelXL[32] refinement package using least squares minimisation. For all structures all non-hydrogen atoms were introduced in difference map positions and refined anisotropically, while hydrogen atoms were introduced in calculated positions and refined on a riding model, except for N-H hydrogen atoms in the model for **9**, which were introduced in difference map positions, and refined isotropically. Solvent was disordered over a special position. During growth, crystals of **6** were in contact with DMF, ethyl acetate, chloroform, acetonitrile, and possibly water. A sensible solvent model could not be achieved, and the solvent contribution was treated with a solvent mask (PLATON SQUEEZE[33].) The solvent contribution was omitted from the formula, and hence was not included in the calculation of other intensive properties (ex. molecular weight; density.) Crystallographic data are summarized in Table S1.

Emission Studies

Electronic absorption spectra were measured with a Varian (Agilent) Cary 500 UV-vis-NIR spectrometer. Emission measurements were made with an Edinburgh Instruments FLSP-920 combined steady-state/time-resolved spectrometer. Solutions for emission quantum yield measurements were prepared with an absorbance of 0.1 at the corresponding excitation wavelength. The samples were then purged with nitrogen for at least 30 min., sealed, and then measured. An appropriate cut-off filter was used for the Φ_{em} measurements to remove the excitation frequency doubling from the recorded emission. Three scans each with a dwell time of 1 sec/nm were averaged.

Electrochemical Studies

Solutions of compounds **1**, **4b**, and **5-7** were freshly prepared in anhydrous dichloromethane (1 mM) with $TBAPF_6$ (0.1 M). The working electrode was a straight Pt wire. The counter electrode was a coiled Pt wire, which was burned before using to ensure it was uncontaminated and not oxidized. The reference electrode was a silver wire that was polished before using. A stock solution of ferrocene (100 mM) with $TBAPF_6$ (0.1 M) was prepared in anhydrous dichloromethane. The ferrocene stock solution was added to the sample in a 1:1 molar ratio to serve as an internal reference. The voltmmograms were measured at 100 mV/s. For the square wave measurements, (pulse height) P_H=25 mV, (pulse width) P_W=50 ms, (step height) S_H=10 mV, scan rate = 100 mV/s parameters were used.

ASSOCIATED CONTENT

Supporting Information

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

NMR, X-ray crystallographic details, electrochemical studies, and DFT calculations. (PDF)

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no conflicts.

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