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Synthesis, Optical Properties, and Electronic Structures of Nucleobase-Containing π-Conjugated Oligomers

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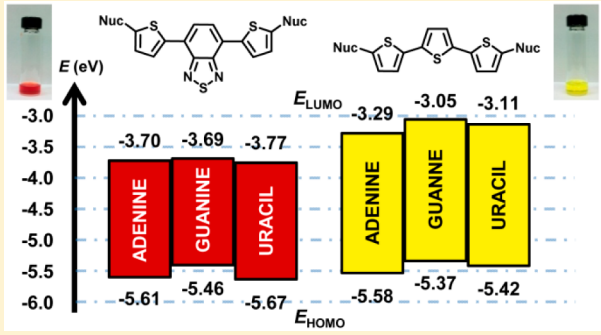
Supporting Information

ABSTRACT: The molecular recognition properties of the nucleobases instruct the formation of complex three-dimensional architectures in natural and synthetic systems; relatively unexplored is their use as building blocks for π-conjugated materials where they might mutually tune electronic and supramolecular structures. Toward this goal, an introductory set (**1a−d** and **2a−d**) of six purine-terminated and two pyrimidine-terminated π-conjugated oligomers has been synthesized and used to develop experimental electronic and photophysical structure−property trends. Unlike 2,2′:5′,2″-terthiophene (TTT) derivatives **2a−d**, intramolecular charge transfer dominates oligomers **1a−d** bearing a 4,7-bisthienylbenzothiadiazole (TBT) spacer due to the strong electron-accepting ability of its benzothiadiazole (BTD) ring. The resulting donor−acceptor−donor systems feature lower HOMO−LUMO gaps than the terthiophene-linked nucleobases (ΔE_g ∼ 1.8 eV vs 2.4 eV based on electrochemical measurements), and the lowest so far for π-conjugated molecules that include nucleobases within the π-framework. Experiments reveal a dependence of photophysical and electronic structure on the nature of the nucleobase and are in good agreement with theoretical calculations performed at the B3LYP/6-31+G** level. Overall, the results show how nucleobase heterocycles can be installed within π-systems to tune optical and electronic properties. Future work will evaluate the consequences of these information-rich components on supramolecular π-conjugated structure.



INTRODUCTION

Semiconductive organic molecules have found applications in electronic and optoelectronic devices, including light emitting diodes,[1] field effect transistors,[2] solar cells,[3] optical sensors,[4] electrochromic devices,[5] and photodetectors.[6] The suitability of π-conjugated organic molecules for these applications generally derives from their structural tunability, light absorption and emission characteristics, and processability from solution.[7] Also intimately linked with the function of π-systems is their supramolecular ordering, in solution and the solid state, that impacts both optical and electronic characteristics (e.g., charge mobility).[8] Substantial previous work has shown how the assembly promoting building blocks of biology can be used to control the three-dimensional ordering of π-conjugated materials and oligomers, in particular. The strategy often involves appending amino acids/peptides,[9] nucleobases/nucleosides,[10] or other bioinspired molecular recognition elements to the π-chromophore periphery[11] where the consequences on optical,[12] electronic,[13] and supramolecular properties can be profound.[14] Not well explored to date is how the nucleobases (i.e., purines and pyrimidines), Nature's own π-building blocks, might be embedded within (as opposed to appended to) π-conjugated frameworks to generate novel opto- and/or electroactive molecules.[13,15] It is in these cases that an intimate relationship between nucleobase π-system structure and function would exist to make the conjugates unique for optoelectronic applications. To date, the concept has only been exploited for relatively simple nucleobases through the work of the Bach,[16] Gottarelli,[17] Spada,[10c,14b,17a,c−e,18] Davis,[18,19] Rivera,[20] and Neogi[21] groups. Along these lines, our lab has shown how purines can be rendered highly fluorescent upon modest structural perturbation to the π-system,[22] making them suitable as the emissive component of relatively efficient blue-violet-UV emitting OLEDs.[23]

Consideration of purines (e.g., adenine and guanine) and pyrimidines (e.g., cytosine and thymine/uracil) as components of extended oligomeric π-systems reveals challenges and opportunities unique from conventionally used heterocycles (e.g., carbazoles, thiophenes, pyridines, etc.). From the design and synthesis standpoint, challenges include the following: (1) What oligomer design best preserves the H-bonding capabilities of the nucleobases? (2) Which synthetic methods can successfully introduce such highly coordinating (i.e., to metals)

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and poorly soluble building blocks to π-frameworks? Regarding opportunities, it is intriguing to consider how the electronic structures of the nucleobases—intensely studied over many years in the context of DNA charge transport[24]—might result in base-specific optical/electronic differences among their derivative π-conjugated oligomers.

As an entry into such π-systems, reported here are the syntheses, optical properties, and electronic structures of two model families of nucleobase-containing π-conjugated oligomers (Figure 1). The overall design preserves the

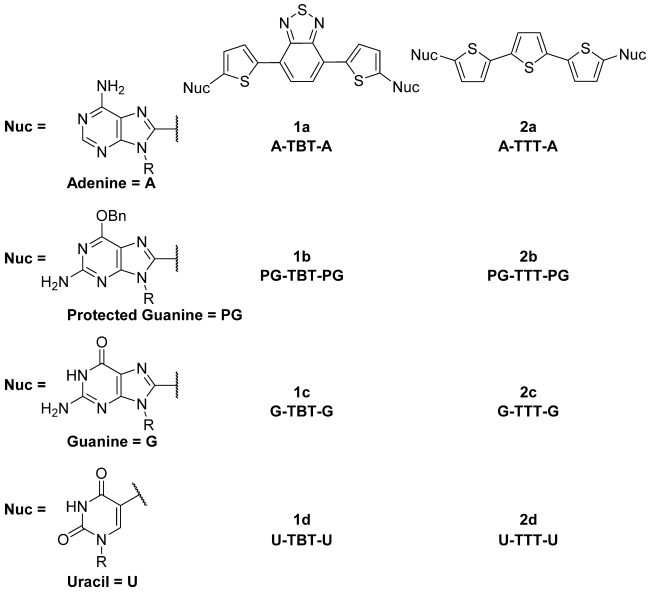


Figure 1. Purine- and pyrimidine-containing π-conjugated targets evaluated in this work. R = 2-ethylhexyl.

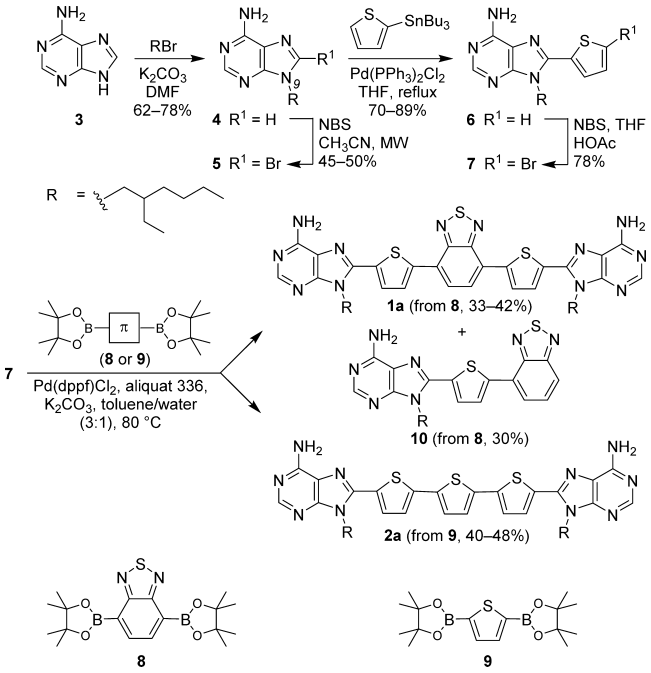
Watson−Crick base pairing edges of the purines or pyrimidines by having the heterocycles installed in terminal positions. The families (**1** and **2**) are distinguished by the intervening π-structure that consists of 4,7-bisthienylbenzothiadiazole (TBT)[25] or terthiophene (TTT),[7a,26] tracks that are (a) familiar from π-functional materials and (b) sufficiently long to afford molecules with optical and electronic characteristics considered attractive for sensing and optoelectronic applications. To address the potentially low solubility of the oligomers, 2-ethylhexyl substituents are introduced in place of the sugars on the nucleobases. This alkyl chain, popular in the π-conjugated materials community, was selected on the basis of a qualitative organic solubility screen (vide infra). Experimental and theoretical (by DFT) analyses have since revealed that the absorption, emission, emission lifetime, fluorescence quantum yields, and electronic properties respond in understandable ways to nucleobase and π-linker electronic structure.

RESULTS AND DISCUSSION

Synthesis. *Selection of Solubilizing Group.* We recognized quickly that the poor solubility of the nucleobases in common organic solvents would necessitate the addition of appropriate solubilizing groups, most conveniently introduced to the position otherwise occupied by the sugar (sugars were not considered due to problematic lability of the N,O-acetal linkage). To guide our selection, we conducted a series of qualitative solubility studies, in chloroform, of uracil substituted at position N(3) with linear (e.g., hexyl, octyl, dodecyl), branched symmetrical (e.g., 2-ethylbutyl), branched asymmetrical (e.g., 2-ethylhexyl), and cyclic (e.g., cyclohexylmethyl) alkyl chains (Table S1, Supporting Information). The results confirmed that the popular 2-ethylhexyl group provided the best solubility among the choices; consequently, this alkyl chain was employed for all of the targets considered in this work (Figure 1). The favorable performance of the 2-ethylhexyl chain is undoubtedly linked to its chiral carbon that generates mixtures of diastereomers (in cases where there are two or more 2-ethylhexyl groups in a molecule) and frustrates solid-state packing. Typically, this stereochemical aspect is ignored, and only recently has its ramifications for thin-film based organic devices been exposed.[27] In this work, targets bearing two 2-ethylhexyl groups (Figure 1) are assumed to exist as a mixture of stereoisomers, but the isomeric composition should not have an effect on photophysical properties in dilute solution.[27a]

Adenine-Terminated Oligomers. The synthesis of adenine-terminated π-conjugated oligomers, **1a** and **2a**, is illustrated in Scheme 1. A solution of adenine **3** in DMF was treated with

Scheme 1. Synthesis of Adenine-Terminated Oligomers 1a and 2a



anhydrous K_2CO_3, followed by addition of *rac*-2-ethylhexyl bromide, yielding both N(7) and N(9) regioisomers of **4** in a 1:3 ratio (determined by ^{1}H NMR). The regiochemistry of the major product was confirmed by ^{1}H−^{13}C gHMBC NMR (see Figures S1 and S2, Supporting Information, for details) where correlation of C(4) (150.4 ppm) and C(8) (142.0 ppm) with the methylene protons (4.02 ppm) of the 2-ethylhexyl group was observed (Figure 2). Bromination at C(8) was then pursued to introduce a handle for subsequent metal-mediated cross-coupling to expand the π-system. Unfortunately, conventional bromination conditions[28] (Table S2, Supporting Information) either failed to generate the product **5** or delivered it in low yields (7−25%). This challenging reaction was improved significantly under microwave conditions (100 W

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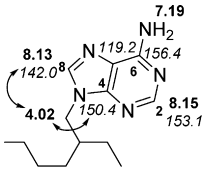


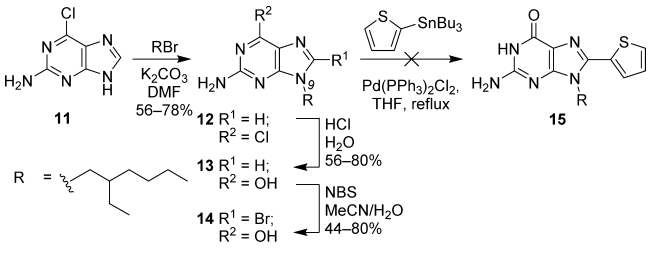
Figure 2. ^{1}H (bold) and ^{13}C (italics) chemical shifts (in ppm) and key $^{1}H-^{13}C$ gHMBC correlations for **4**.

at 75 °C); a mixture of **4** and NBS in acetonitrile afforded **5** in 45−50% yield in just 20 min.

Initial attempts (not shown) to couple 8-bromoadenine **5** to bisstannylated π-spacers (e.g., 5,5″-bis(tributylstannyl)-2,2′:5′,2″-terthiophene to afford **1a**) in one step were not successful (starting material **5** was recovered). These observations prompted an iterative approach. Bromoadenine **5** was first reacted with 2-(tributylstannyl)thiophene, following a literature procedure,[29] to afford intermediate **6** in excellent yield. Subsequent bromination of the thiophenyl 2-position with NBS furnished **7** in good yield. A final Suzuki coupling of **7** to boronic esters **8** and **9**, synthesized according to literature procedures,[30] resulted in the formation of **1a** (33−42%) and **2a** (40−48%), respectively. The monocoupling product **10** was also isolated from the reaction of **7** and **8** in 30% yield. Different palladium-based catalysts were screened to optimize the Suzuki couplings. Those bearing bidentate ligands (e.g., $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$) that enforce a cis geometry between the aryl fragments and facilitate reductive elimination offered higher yields and fewer side products compared to those with monodentate ligands (e.g., tri-*o*-tolylphosphine, dibenzylideneacetone (dba), etc.).

Guanine-Terminated Oligomers. Synthesis of guanine derivatives **1c** and **2c** initially followed the adenine-based conjugated oligomer syntheses starting from guanine (Scheme 2). Alkylation of 2-amino-6-chloropurine **11**, obtained from

Scheme 2. Attempted Synthesis of 15

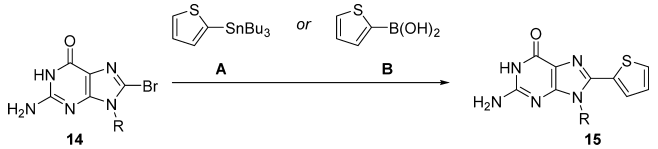


treatment of guanine with $POCl_3$ in DMF,[31] with *rac*-2-ethylhexyl bromide afforded both N(7) and N(9) regioisomers of **12** in an ∼1:3 ratio (determined by ^{1}H NMR). The regiochemistry of **12** was confirmed by $^{1}H-^{13}C$ *g*HMBC NMR (Figures S3 and S4, Supporting Information). Dilute acid hydrolysis of **12** furnished guanine intermediate **13**, which was subsequently brominated at C(8) with NBS to yield **14**. Unfortunately, cross-coupling of **14** with 2-(tributylstannyl)-thiophene under the Stille conditions[29] previously used for adenine intermediate **7** did not afford the target **15**.

Several cross-coupling conditions were attempted with **14** and either 2-(tributylstannyl)thiophene (**A**) or 2-thienylboronic acid (**B**). These ranged from Stille couplings without (entry 1, Table 1) or with additives (entries 2 and 3, Table 1), to Suzuki couplings using conventional (entries 4 and 5, Table 1) and microwave heating (which yielded incomplete reactions) (entry 6, Table 1). Only Stille conditions (entry 3, Table 1) with triphenylbismuth (5%)[32] both successfully and reproducibly allowed cross-coupling of **14** with stannylthiophene (affording **15** in 66% yield). Presumably, the longer Bi−Pd bond (versus the P−Pd bond) facilitates activation of the catalyst and reduces the reaction time.[32] The same conditions were attempted (Scheme 3) for coupling **14** and a bis(trimethylstannylthienyl)-benzothiadiazole derivative **17** (prepared efficiently from 4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole **16**) to provide **1c** directly; however, these conditions led to decomposition of the benzothiadiazole reagent. Bromination of **15**, followed by direct coupling to **8**/**9** (or their bis(stannyl) versions, of which bis(trimethylstannyl)benzo[*c*][1,2,5]thiadiazole has not been reported), was not pursued given the general difficulty manipulating the parent guanine derivatives in cross-coupling reactions (vide infra). As for the poorly performing Suzuki conditions (Table 1), the work of Shaughnessy et al. suggests that the deprotonation of the acidic N(1) proton of the guanine moiety to give a highly coordinating anion for the palladium catalyst (Pd(II) and Pd(0)) could be to blame (Scheme 4).[33]

To circumvent the above challenges, we developed a synthetic route using a protected guanine derivative (Scheme 5). Along these lines, **18** was prepared in 64−84% yield by the reaction of **12** and benzyl alcohol in the presence of K_2CO_3 and a catalytic amount of DABCO.[34] Bromination of **18** was then achieved using NBS in DMF to afford **19** in 70−85% yield; the 8-bromo derivative **19** then underwent Stille cross-coupling with 2-(tributylstannyl)thiophene in the presence of triphenylbismuth to generate **20** in excellent yields (87−97%). Subsequent bromination of **20** using NBS in THF/AcOH

Table 1. Optimization of the Cross-Coupling Conditions to Prepare 15



entry[a]	coupling partner	catalyst (equiv)	solvent	*T*	conditions/additives	% yield **15**
1[29]	**A**	$Pd(PPh_3)_2Cl_2$ (0.1)	THF	reflux		trace
2[36]	**A**	Pd_2dba_3 (0.1)	NMP	100 °C	$AsPh_3$ (10%)	N.R.[b]
3[32]	**A**	$Pd(PPh_3)_4$ (0.2)	xylenes	reflux	Ph_3Bi (5%)	66
4[30a]	**B**	$Pd(dppf)Cl_2$ (0.2)	toluene-water (3:1)	80 °C	Aliquat 336, K_2CO_3	N.R.[b]
5[37]	**B**	$Pd(OAc)_2$ (0.3)	THF	reflux	Na_2CO_3, $(o\text{-tol})_3P$	N.R.[b]
6[37]	**B**	$Pd(OAc)_2$ (0.3)	acetonitrile−DMF−water (1:1:2)	120 °C	MW, Na_2CO_3, $(o\text{-tol})_3P$	trace

[a]Lead references are given for the conditions used based on similar purine derivatives as starting materials. [b]No reaction.

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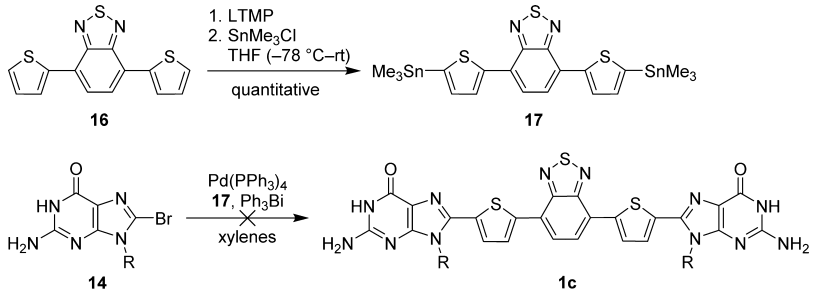
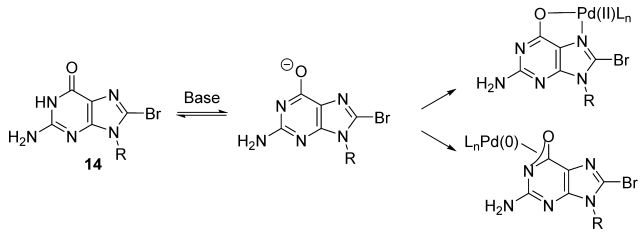
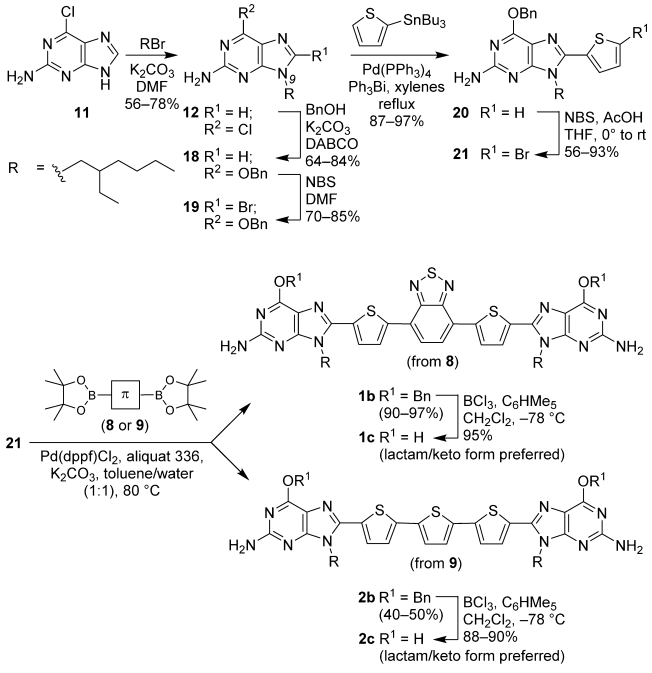
Scheme 3. Attempted Synthesis of 1c under Stille Cross-Coupling Conditions (R = 2-Ethylhexyl)



Scheme 4. Possible Coordination of Deprotonated 14 to the Pd Catalyst under Basic Conditions



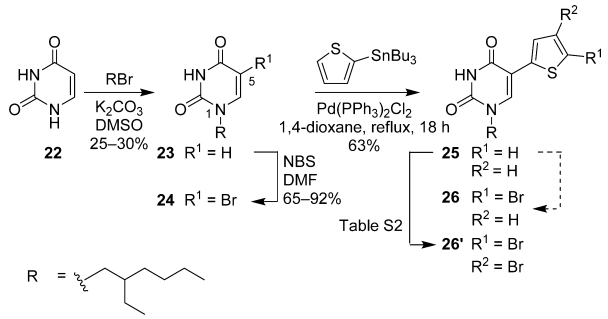
Scheme 5. Synthesis of Guanine-Containing Oligomers 2c and 3c



provided versatile intermediate **21**, which was reacted with **8** and **9** under Suzuki cross-coupling conditions to furnish **1b** (90–97%) and **2b** (40–50%), respectively. The lower yield of **2b** reflects its required purification by column chromatography. Final treatment of **1b** and **2b** with BCl_3 in the presence of pentamethylbenzene as a cation scavenger[35] afforded guanine derivatives **1c** and **2c**, correspondingly (Scheme 5).

Uracil-Terminated Oligomers. Synthesis of uracil derivatives was initiated following the same approach employed for the purines (Scheme 6). Uracil **22** was treated with K_2CO_3 in DMSO, followed by addition of *rac*-2-ethylhexyl bromide at 40 °C, to generate the N(1)-alkylated product **23** in modest yield (25–30%). Subsequently, a solution of **23** and NBS in DMF

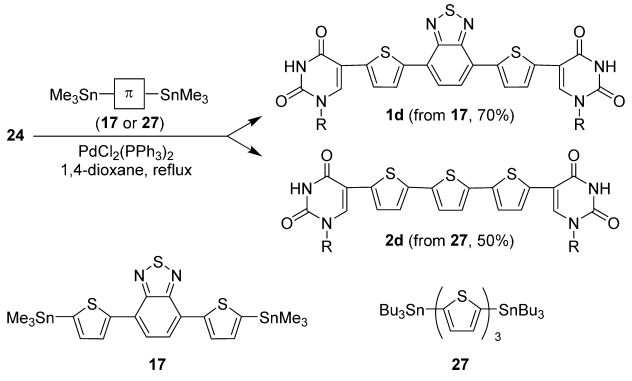
Scheme 6. Attempted Synthesis of 26



was stirred for 30 min at rt to afford **24** (65–92%). Stille coupling with 2-(tributylstannyl)thiophene generated the product **25** as a white solid in 63% yield after overnight heating at reflux. Worth noting, the acidic amidic hydrogen was not problematic in this case given the nonbasic Stille conditions. Bromination at C(5) of the thiophene ring of **25** did not proceed as expected and generated a dibrominated product **26′** under several conditions (Table S3, Supporting Information). To circumvent this issue, 4,7-bis(5-(trimethylstannyl)thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole **17**[38] and 5,5″-bis(tributylstannyl)-2,2′:5′,2″-terthiophene **27**[39] were prepared following literature procedures, then subjected to Stille coupling with 5-bromouracil **24** to furnish the target compounds **1d** and **2d** in 70% and 50% yield, respectively (Scheme 7). That this more direct synthetic approach is possible for uracil, but not the adenine or guanine derivatives, speaks to a structural (and associated electronic) dependency that is currently not completely understood.

Cytosine-Terminated Oligomers. Conspicuously absent from Figure 1 are cytosine derivatives that proved problematic

Scheme 7. Synthesis of Uracil-Containing Oligomers 1d and 2d



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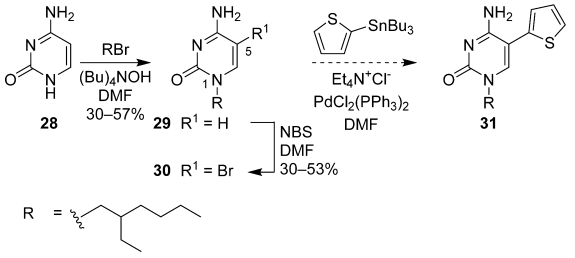
to prepare. To wit, cytosine **28** was treated (Scheme 8) with tetrabutylammonium hydroxide in DMF at rt, followed by

Scheme 8. Attempted Synthesis of 31



addition of *rac*-2-ethylhexyl bromide, to afford 1-(2-ethylhexyl)cytosine **29** (30–57% yield).[40] Halogenation of **29** employing NBS in DMF at rt for 30 min resulted in the corresponding 5-bromo derivative **30** in moderate yields.[41] All attempts to extend the conjugation of cytosine by adding a thienyl group at position C(5) failed to provide the desired product **31** using either Stille conditions[42] or other[43] reported approaches for cytosine derivatives. Iodination of C(5) is currently under investigation as an entry to these targets.

Thermal Properties. Given their relevance to potential downstream applications, the thermal stability of the target compounds was assessed by thermal gravimetric analysis (TGA). The adenine derivatives **1a** and **2a** showed loss of 5% of the original compound weight at relatively high temperatures, 239 and 394 °C, respectively (Figures S5 and S9, Supporting Information). High thermal stability was also observed for **1b** and **2b**, which showed loss of 5% of the original compound weight at 345 and 320 °C (Figures S6 and S10, Supporting Information), respectively. On the other hand, **1c** and **2c** tended to trap solvent molecules, as evidenced by enhanced thermal stability upon longer vacuum drying of the solids prior to measurement (Figures S7 and S11, Supporting Information). However, the major transitions of **1c** and **2c** seem to be comparable to **1b** and **2b**. Finally, compounds **1d** and **2d** exhibited good thermal stability with loss of 5% of the original compound weight at 283 and 352 °C, respectively (Figures S8 and S12, Supporting Information).

Optical Properties. The UV–vis absorption spectra of **1a–d** and **2a–d** in solution were collected to establish relationships between π-conjugated (and nucleobase) structure and photophysical properties. Absorption spectra were measured in 1,4-dioxane ($E_T(N)$ = 0.164) and DMF ($E_T(N)$ = 0.386),[44] solvents with differing polarity and the ability to dissolve the nucleobase-terminated oligomers. In 1,4-dioxane, the absorption spectra of **1a–d** displayed two absorption bands over a range of 350–515 nm (Figure 3 and Table 2). The bands at

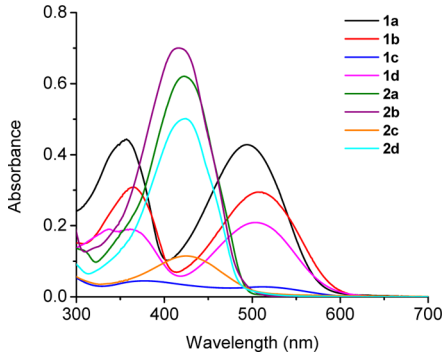


Figure 3. Absorption spectra (1.5×10^{-6} M) for **1a–d** and **2a–d** in 1,4-dioxane.

shorter wavelength, 357, 363, 372, and 361 nm, correspond to π–π^* transitions of the **1a**, **1b**, **1c**, and **1d** chromophores, respectively. The longest wavelength absorption bands at 494, 505, 513, and 503 nm are consistent with donor–acceptor internal charge transfer (ICT) and the donor–acceptor–donor (DAD) structure (vide infra). On the other hand, the absorption spectra of **2a**, **2b**, **2c**, and **2d** displayed a single band at 423, 416, 425, and 424 nm, respectively, when compared to the benzothiadiazole (BTD) derivatives **1**. In DMF, all absorption peaks were shifted to slightly longer wavelengths (Figure 4 and Table 2). This solvatochromism, in

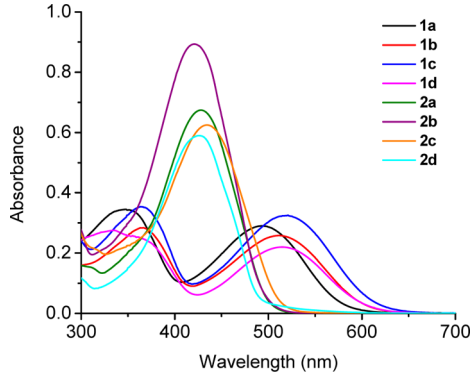


Figure 4. Absorption spectra (1.5×10^{-6} M) for **1a–d** and **2a–d** in DMF.

Table 2. Absorption Properties of 1 and 2 in 1,4-Dioxane and DMF[a]

	1,4-dioxane		DMF	
compound	abs λ_{max} (nm)[b]	$\varepsilon \times 10^4$ (M^{-1} cm^{-1})	abs λ_{max} (nm)[b]	$\varepsilon \times 10^4$ (M^{-1} cm^{-1})
1a	494	2.9 ± 0.1	493	1.9 ± 0.2
1b	505	1.9 ± 0.1	510	1.7 ± 0.1
1c	513	0.20 ± 0.08	516	2.1 ± 0.5
1d	503	1.4 ± 0.1	513	1.4 ± 0.2
2a	423	4.1 ± 0.2	428	4.5 ± 0.4
2b	416	4.6 ± 0.8	422	5.9 ± 0.3
2c	425	0.70 ± 0.04	434	4.1 ± 0.1
2d	424	3.0 ± 0.1	426	3.9 ± 0.2

[a]All measurements were performed at room temperature and at 15×10^{-6} M. [b]Lowest energy absorption maxima. abs λ_{max} (nm) ± 1 nm.

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response to increased solvent polarity, is consistent with a larger dipole moment of the chromophore in the excited state than in the ground state.

It is noteworthy that **1a,b,d** (Figures S13, S14, S16) and **2a,b** (Figures S17, S18) (Supporting Information) clearly follow the Beer–Lambert law for concentrations up to 30 × 10^{-6} M in 1,4-dioxane, which argues against aggregation in the ground state. Such is not necessarily the case for guanine derivatives **1c** and **2c**, and uracil derivative **2d**, in 1,4-dioxane (Figures S15, S19, and S20, Supporting Information). When comparing the absorbance spectra of **1a–d** and **2a–d** in both 1,4-dioxane and DMF, guanine derivatives **1c** and **2c** exhibited the most red-shifted absorption bands. These results are consistent with the stronger electron-donating character of the guanine nucleobase (guanine has the lowest calculated ionization potential among the nucleobases: 8.66, 7.95, and 7.52 V for uracil, adenine, and guanine, respectively[45]); the observed absorbance red shift can also be due to aggregation in 1,4-dioxane solution (vide supra). Overall, the nucleobase identity tunes the absorption maxima up to 20 nm within each series, best read out from the DMF absorption data. Furthermore, the molar extinction coefficient observed for the low-energy absorption of **1a–d** is reduced by at least a factor of 2 compared to that of the absorption of **2a–d** (see Table 2).

The emission spectra of **1a–d** in 1,4-dioxane showed single structureless bands at 618, 631, 640, and 640 nm, respectively (Figure 5 and Table 3). Unlike the absorbance, the emission profiles of **1c** and **2c** showed no signs of aggregation since the measurements are performed at lower concentrations. Vibrational progressions were observed in the emission spectra of **2a–d**. The structureless emission spectra of **1a–d** suggest that the long-wavelength emission arises from an internal charge-transfer (ICT) state. Larger Stokes shifts were observed for **1a–d** (124, 126, 127, and 137 nm, respectively) as compared to **2a–d** (67, 64, 79, and 60 nm, respectively), thus reflecting more structural reorganization of **1a–d** upon photoexcitation.[46]

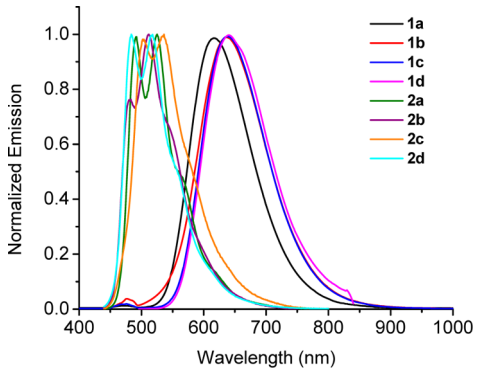

Figure 5. Emission spectra for **1a–d** and **2a–d** in 1,4-dioxane (1–3 × 10^{-6} M; λ_{ex} = 476 nm for **1**; λ_{ex} = 430 nm for **2**).

The fluorescence quantum yields measured for **2a–d** are strikingly lower than those for the **1a–d** oligomers (Table 3), which is in contrast with the band gap law.[47] This may result from the sulfur atoms of the terthiophene-containing oligomers that promote intersystem crossing to the triplet manifold via spin–orbit coupling.[47a,48] Further insight into the fluorescence behavior could be obtained from fluorescence lifetime measurements (Figures S29–S36, Supporting Information). Time-resolved fluorescence decay profiles of all compounds were carried out in 1,4-dioxane. The decay dynamics were determined at an excitation wavelength of 375 nm, and the decays were monitored at the respective emission maxima, 570 nm for **1a–d**, and 475 nm for **2a–d**. The decay data for oligomers **1a–d** could be fit to a single exponential, and these oligomers possessed similar and relatively long decay lifetimes (τ_F ~ 4–6 ns; Table 3). In contrast, **2a–d** showed much shorter lifetimes (τ_F ~ 0.5–0.9 ns), and the data for **2b,c** were better fit using a double exponential decay function. The radiative decay rates (k_r) for **1a–d** calculated as $k_r = \varphi_F/\tau_f$ are in the range of (0.6–1.3) × 10^7 s^{-1}. The lifetimes and radiative decay rates for **1a–d** are typical for π-conjugated oligomers with strongly allowed long-axis polarized π,π^* singlet excited states.[49] By contrast, compounds **2a–d** have fluorescence lifetimes that are one order of magnitude lower than the benzothiadiazole series, and the corresponding radiative rates are higher (1.1–2.4 × 10^7 s^{-1}). The significant difference in fluorescence lifetime and radiative rates for **1a–d** and **2a–d** likely reflects the fact that the singlet excited state in the TBT oligomers has a significant degree of charge-transfer character, and it adds support to the notion that the BTD unit is a strong acceptor.[47a]

Electrochemical Properties. The redox properties of **1a–d** and **2a–d** were investigated by cyclic voltammetry (CV) in DMF with NBu_4PF_6 as the supporting electrolyte (Table 4 and Table S4, Supporting Information). Differential pulse voltammetry (DPV) data were also obtained, as DPV offers better sensitivity than CV and leads to steeper peak onsets due to the

Table 3. Emission Properties of 1 and 2 in 1,4-Dioxane[a]

compound	em λ_{max} (nm)[b]	Stokes shift (nm)	φ_F[c]	τ_F (ns)[d]	$k_r = \varphi_F/\tau_f \times 10^7$ (s^{-1})
1a	618	124	0.64	4.83[e]	1.32
1b	631	126	0.38	3.92[e]	0.97
1c	640	127	0.25	3.94[e]	0.63
1d	640	137	0.33	5.95[e]	0.55
2a	490, 524	67	0.15	0.63[e]	2.38
2b	480, 513	64	0.11	0.50 (66%)[f]	2.22
2c	504, 536	79	0.10	0.89 (52%)[f]	1.12
2d	484, 517	60	0.19	0.88[e]	2.16

[a]All measurements were performed at room temperature. [b]All experiments were performed using optical densities ≤ 0.1 at the excitation wavelength (λ_{ex} = 476 nm for **1**; λ_{ex} = 430 nm for **2**), so generally 5–10 × 10^{-6} M. [c]Fluorescence quantum yields are relative to the quantum yield of either Rhodamine B in absolute ethanol (φ_F = 0.49; for **1a–d**) or Fluorescein in 0.1 M NaOH (φ_F = 0.79; for **2a–d**). [d]Theoretical exponential decay curves are fitted with the instrument response function, and the best fit is obtained when χ^2 = 0.9–1.1. [e]Fluorescence lifetime first-order decay. [f]Fluorescence lifetime second-order decay with contribution percentage to the lifetime shown in parentheses.

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Table 4. Electronic Properties of 1 and 2

	experimental					DFT calculations[a]		
compound	HOMO (eV)[b]	LUMO (eV)[b]	ΔE_g electrochemical (eV)	ΔE_g optical (eV) [1,4-dioxane][c]	ΔE_g optical (eV) [DMF][d]	HOMO (eV)	LUMO (eV)	ΔE_g (eV)
1a	−5.61	−3.70	1.91	2.10	2.14	−5.50	−3.21	2.29
1b	−5.49	−3.71	1.78	2.10	2.07	−5.15	−2.96	2.19
1c	−5.46	−3.69	1.77	2.01	2.01	−5.16	−2.92	2.24
1d	−5.67	−3.77	1.90	2.11	2.07	−5.45	−3.12	2.33
2a	−5.58	−3.29	2.29	2.53	2.48	−5.40	−2.60	2.80
2b	−5.46	−3.11	2.35	2.56	2.52	−5.07	−2.30	2.77
2c	−5.37	−3.05	2.32	2.49	2.43	−5.07	−2.25	2.82
2d	−5.42	−3.11	2.31	2.55	2.54	−5.32	−2.54	2.78

[a]All 2-ethylhexyl groups have been replaced by methyl groups for the calculations. Geometry optimization and calculation of the HOMO and LUMO energies was performed at the B3LYP/6-31+G** level. [b]Estimated HOMO and LUMO energy levels (relative to vacuum) based on electrochemical potentials (E_{onset}^{ox} and E_{onset}^{red}, respectively) determined from the DPV experiments in DMF (0.1 M $TBAPF_6$). See the Supporting Information for electrochemistry details. [c]Determined based on UV absorption data in 1,4-dioxane. [d]Determined based on UV absorption data in DMF.

sharper current response occurring near the E^o region (due to the selective extraction of Faradaic current).[50] The peak shapes seen in DPV also shed light on the redox behavior of the molecules. Compared to quasi-reversible and irreversible systems, truly reversible electrochemical events exhibit sharper, more symmetrical peaks.[50]

The two following equations were used to estimate the HOMO and LUMO levels from the DPV data.[50,51]

$$E_{HOMO} = -(E_{onset}^{ox} + 5.1)\ \text{eV}$$

$$E_{LUMO} = -(E_{onset}^{red} + 5.1)\ \text{eV}$$

where E_{onset}^{ox} and E_{onset}^{red} are the onset oxidation and reduction potentials measured for the compounds in solution versus the Fc/Fc^+ reference.

Cyclic voltammetry revealed that the oligomers **1a−c** and **2a−c** undergo a single irreversible oxidation, commonly described in the literature for purine derivatives,[23b,52] while the cyclic voltammograms of oligomers **1d** and **2d** indicated two irreversible oxidations within the accessible solvent window (Figures S37−S44, Supporting Information). Within the TBT series, adenine **1a** and protected guanine **1b** derivatives display three reversible or quasi-reversible reduction bands. Meanwhile, **1c** and **1d** show only one reversible reduction observable within the solvent window. Likewise, two reversible reduction bands are characteristic of **2a** and **2b**, while **2c** and **2d** possess only one. The strong electron-accepting character of the BTD moiety was verified by the positive shift of the onsets of the reduction bands of oligomers **1a−d** by ca. 410−640 mV (DPV) with respect to their terthiophene analogues **2a−d**, resulting in lower corresponding LUMO values for **1a−d** (Table 4). While the oxidation potentials and the respective HOMO values of **1a−d** and **2a−d** are comparable, a certain degree of tunability of the HOMO level of the oligomer can be attained by changing the nucleobase structure from adenine, to 2-amino-6-(benzyloxy)-9*H*-purine (protected guanine), to guanine, or to uracil. Consistent with the literature,[53] for example, the redox potentials indicate that the unprotected guanine is the strongest electron-donor among the nucleobases with the respective oligomers having oxidation onsets at as low as 0.36 and 0.27 V vs Fc/Fc^+ (DPV values) for **1c** and **2c**, respectively. Interestingly, the nucleobase structure has little effect on the reduction onsets and LUMO values in the TBT series demonstrating that the LUMO is dominated by the strong BTD acceptor. Although compounds within families **1** and **2** have similar electrochemically derived HOMO−LUMO gaps (ΔE_g = 1.77−1.91 eV for **1a−d**; ΔE_g = 2.29−2.35 eV for **2a−d**), the members differ slightly in their HOMO and LUMO values speaking to optical and electronic tunability. Lastly worth noting, the electrochemical and optical data trends are consistent. Guanine derivatives **1b** and **1c**, for example, show the most bathochromically shifted absorbance bands and also the smallest electrochemically determined ΔE_g values. Likewise, both the electrochemically and the optically (ΔE_g = 2.01−2.14 eV for **1a−d**; ΔE_g = 2.43−2.54 eV for **2a−d**) derived HOMO−LUMO gaps of **1** are reduced by ∼0.4−0.5 eV relative to **2**.

Electronic Structure Calculations. The HOMO and LUMO energies of **1a−d** and **2a−d** were calculated, and the structural geometries were optimized at the B3LYP/6-31+G** level of theory (as implemented in Gaussian 09[54]). In all cases, the 2-ethylhexyl groups were truncated to methyl groups to reduce computational time, since they do not significantly affect the equilibrium geometries or electronic properties. The oligomers are predicted to be quite planar. Using **1a** and **2a** as representative examples (Figure 6), the aryl−aryl dihedral angles range from 0−1.1° and 2.4−2.8°, respectively. Assignment of the oligomer conformations as global minima was possible through calculations using truncated versions, like **10** (see the Supporting Information and Figure S45 for details).

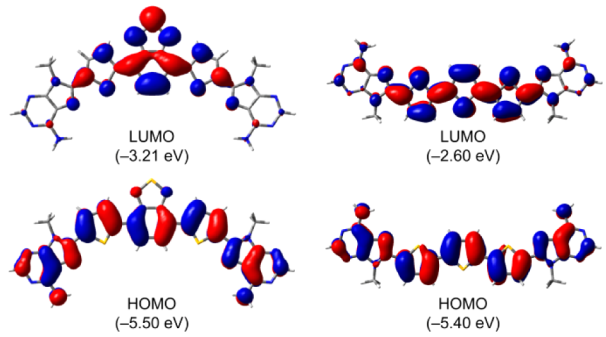

Figure 6. Calculated HOMO and LUMO plots for **1a** (left) and **2a** (right) based on B3LYP/6-31+G** calculations. 2-Ethylhexyl groups have been truncated to methyl groups for the calculations.

Representative frontier MO plots are depicted in Figure 6 for **1a** (plots for the remaining compounds can be found in Figures S46−48, Supporting Information). The LUMO is concentrated

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on the benzothiadiazole unit, while the HOMO is delocalized on the π-conjugated backbone. The well-separated HOMO and LUMO orbital coefficients indicate that the transition between them can be considered as a charge-transfer transition.[55] For **2a**, the MO constructs suggest that there is significant overlap between strongly delocalized HOMO and LUMO wave functions. The electronic structure should result in a higher oscillator strength; this is reflected by the higher extinction coefficients for **2a**−**d** mentioned earlier (Table 2).[56] As a result, both the HOMO and LUMO energy levels as well as the HOMO−LUMO gap of **1a** are decreased relative to **2a**. The computed HOMO and LUMO energies, and corresponding ΔE_g values, of all compounds are summarized in Table 4.

Finally, the computational studies show that the observed differences in ΔE_g within each series of compounds (i.e., **1a**−**d** and **2a**−**d**) are based solely on the exchange of the nucleobase core; for **1a**−**d**, ΔE_g changes from 2.23, 2.19, to 2.33 eV by simply swapping the nucleobase from adenine **1a**, to guanine **1c**, to uracil **1d**, respectively. From the calculated energy levels of the parent nucleobases (see Figure S49, Supporting Information, for details), the guanines (protected and unprotected) should be the strongest donors[53] and uracil should be the weakest; this theoretical observation is nicely reproduced in the experimental data (vide supra) where **1c** boasts a lower HOMO−LUMO gap than **1d** within the TBT systems due to the modulated strength of the donor−acceptor interaction.

CONCLUSIONS

The DNA/RNA bases (A, C, G, T/U) are unique heterocycles to consider for π-conjugated materials design as they intimately merge π-electron function with predictable pairwise hydrogen bonding motifs. Toward developing bioinformed and functional π-conjugated materials, we have synthesized two families of nucleobase-containing π-oligomers and fully characterized their photophysical and electronic properties with respect to nucleobase and π-backbone structure. Synthetic approaches have been established to navigate the inherent synthetic challenges associated with using "sticky" and aggregating purines and pyrimidines as π-building blocks in Pd-catalyzed cross-coupling reactions. Protocols have specifically allowed addition of three (A, G, U) of the nucleobase heterocycles to the terminal positions of standard thiophene-containing π-conjugated sequences; attempts to prepare cytosine (C) derivatives remain in progress.

Structure−property relationships for the nucleobase-containing π-conjugated oligomers have emerged from a combination of experimental spectroscopic data and DFT calculations. The absorption and emission properties, emission lifetimes, and fluorescence quantum yields respond in understandable ways to both nucleobase and π-backbone electronic structure. For example, guanine-terminated derivatives (G-TBT-G and G-TTT-G) exhibit the most bathochromically shifted absorption, consistent with the nucleobase's good electron-donating character compared to A and U. Despite having lower HOMO−LUMO gaps, the fluorescence quantum yields and lifetimes of the TBT-linked nucleobases are significantly improved over the terthiophene (TTT) family. The redox behavior of the oligomers could be evaluated by CV and DPV, and the HOMO and LUMO energies estimated from the data show a dependence on the nature of the nucleobase and are in good agreement with electronic structure calculations performed at the B3LYP/6-31+G** level.

In other work, we are showing how π-conjugated oligomers that combine intrinsic light absorption and hydrogen bond directed self-assembly properties are interesting candidates as organic solar cell materials.[57] With an understanding of how a nucleobase π-structure can confer tunable optical and electronic properties to traditional π-conjugated oligomers, we are poised to evaluate the consequences of "base-pairing" on optoelectronic thin film structure and function. Work along these lines is underway and will be reported in due course.

EXPERIMENTAL SECTION

General Information. Reagents and solvents were purchased from commercial sources and used without further purification unless otherwise specified. THF, diethyl ether, CH_2Cl_2, and DMF were degassed in 20 L drums and passed through two sequential purification columns (activated alumina; molecular sieves for DMF) under a positive argon atmosphere. Tetrakis(triphenylphosphine) palladium(0), *trans*-bis(triphenylphosphine) palladium(II) chloride, and [1,1′-bis(diphenylphosphino)ferrocene]dichloro palladium(II) (complex with dichloromethane, and [Pd(dppf)Cl_2·CH_2Cl_2]) were purchased from Strem Chemicals or Sigma-Aldrich and used as received. Thin-layer chromatography (TLC) was performed on SiO_2-60 F254 aluminum plates with visualization by UV light or staining. Flash column chromatography was performed using SiO_2-60, 230−400 mesh. Melting points (mp) were determined on an electrothermal melting point apparatus. $^1H(^{13}C)$ NMR spectra were recorded on 300(75) MHz or 500(125) MHz spectrometers as specified. Chemical shifts (δ) are given in parts per million (ppm) relative to TMS and referenced to residual protonated solvent ($CDCl_3$: δH 7.26 ppm, δC 77.23 ppm; DMSO-d_6: δH 2.50 ppm, δC 39.50 ppm). Abbreviations used are s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sep (septet), b (broad), and m (multiplet). ESI- and ESI-TOF-MS spectra were recorded on FTICR and TOF spectrometers, respectively. EI-, CI-, and DIP-CI-MS spectra were recorded on a single quadrupole spectrometer. Microwave assisted reactions were carried out with a single mode cavity Discover Microwave Synthesizer (CEM corporation, NC). The following compounds have been prepared using literature procedures: 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzo[*c*][1,2,5]thiadiazole **8**,[30a] 2,5-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene **9**,[30b] 4,7-di(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole **16**, 4,7-bis(5-(trimethylstannyl)-thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole **17**,[39] and 5,5″-bis(trimethylstannyl)-2,2′:5′,2″-terthiophene **27**.[38]

Details of the solubility studies, $^1H-^{13}C$ gHMBC analysis, TGA, photophysical measurements, electrochemistry, and computations can be found in the Supporting Information.

Synthesis of Adenine-Terminated Oligomers. *(±)-9-(2-Ethylhexyl)-9H-purin-6-amine (**4**).* *rac*-2-Ethylhexyl bromide (2.00 mL, 11.0 mmol) was added to a suspension of adenine (1.00 g, 7.40 mmol) and K_2CO_3 (3.11 g, 22.2 mmol) in dry DMF (50 mL). The resulting suspension was stirred for 20 h at rt under argon atmosphere. The insoluble solid was filtered, and the filtrate was evaporated to give a crude white solid, which was purified by column chromatography with gradient elution (MeOH:CH_2Cl_2 3:97 to 5:95) to afford the product as a white solid (1.06 g, 62%). mp 153−156 °C; ^1H NMR (500 MHz, DMSO-d_6): δ 8.12 (s, 1H), 8.11 (s, 1H), 7.17 (s, 2H), 4.03 (d, *J* = 7.5 Hz, 2H), 1.92 (sep, *J* = 6.5 Hz, 1H), 1.21−1.18 (m, 8H), 0.85−0.79 (m, 6H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 155.9, 152.3, 149.8, 141.2, 118.6, 46.3, 38.8, 29.7, 27.8, 23.2, 22.3, 13.8, 10.2; HRMS (ESI) calcd for $C_{13}H_{22}N_5$ $[M + H]^+$: 248.1875, found: 248.1876.

*(±)-8-Bromo-9-(2-ethylhexyl)-9H-purin-6-amine (**5**).* A suspension of NBS (0.76 g, 4.3 mmol) and **4** (0.50 g, 2.1 mmol) in dry CH_3CN (5 mL) was irradiated by microwave (100 W, 75 °C) for 20 min. The solvent was evaporated under reduced pressure, and the crude solid was purified by column chromatography (EtOAc:hexanes, 1:1) to afford **5** as a pale yellow solid (0.32 g, 1.1 mmol, 50%): mp 167−168 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 8.32 (s, 1H), 5.63 (s, 2H), 4.08 (d, *J* = 7.5 Hz, 2H), 2.08−2.04 (m, 1H), 1.30−1.25 (m, 8H), 0.93−0.84 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.6, 153.0, 151.8,

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127.6, 119.9, 48.5, 39.2, 30.4, 28.5, 23.8, 23.0, 14.0, 10.6; HRMS (ESI) calcd for $C_{13}H_{21}BrN_5$ $[M + H]^+$: 326.0980, found: 326.0979.

(±)-9-(2-Ethylhexyl)-8-(thiophen-2-yl)-9H-purin-6-amine (**6**). 2-(Tributylstannyl)thiophene (0.50 mL, 1.6 mmol) was added to a solution of **5** (0.10 g, 0.31 mmol), and $Pd(PPh_3)_2Cl_2$ (0.021 g, 0.031 mmol) in degassed THF (5 mL). The resulting mixture was heated to reflux for 16 h. The solvent was removed under reduced pressure. The crude mixture was purified by column chromatography (EtOAc:hexanes, 40:100 → 100:0) to afford the title compound as a beige solid (0.083 g, 70%): mp 164−167 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.56 (dd, J = 3.9; 1.2 Hz, 1H), 7.53 (dd, J = 5.1; 1.2 Hz, 1H), 7.19 (dd, J = 5.4; 3.9 Hz, 1H), 5.72 (s, 2H), 4.34 (d, J = 7.8 Hz, 2H), 1.96−1.92 (m, 1H), 1.26−1.17 (m, 8H), 0.83−0.78 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 152.8, 152.3, 145.7, 132.1, 128.7, 128.3, 128.0, 119.4, 47.7, 39.1, 30.3, 28.3, 23.8, 23.1, 14.1, 10.6; HRMS (ESI) calcd for $C_{17}H_{24}N_5S$ $[M + H]^+$: 330.1752, found: 330.1754.

(±)-8-(5-Bromothiophen-2-yl)-9-(2-ethylhexyl)-9H-purin-6-amine (**7**). NBS (0.082 g, 0.46 mmol) was added over 2 h to a solution of **6** (0.10 g, 0.30 mmol) in THF (2 mL) and glacial AcOH (2 mL) at 0 °C. The solution was stirred for an additional 2 h at rt and was then diluted with EtOAc (50 mL). The organic layer was washed with H_2O (3 × 25 mL) and brine and was dried over Na_2SO_4 (anhyd) to yield **7** as a beige solid (0.097 g, 78%): mp 150 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ 0. 85−0.80 (m, 6H), 1.26−1.19 (m, 8H), 1.95 (m, 1H), 4.30 (d, J = 7.8 Hz, 2H), 5.64 (s, 2H), 7.14 (d, J = 3.9 Hz, 1H), 7.29 (d, J = 4.2 Hz, 1H), 8.36 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 10.7, 14.2, 23.1, 23.9, 28.5, 30.5, 39.2, 47.9, 116.3, 119.6, 128.3, 131.0, 134.1, 144.6, 152.4, 153.1, 155.3; HRMS (ESI) calcd for $C_{17}H_{23}BrN_5S$ $[M + H]^+$: 410.0837, found: 410.0834.

8-(5-(Benzo[c][1,2,5]thiadiazol-4-yl)thiophen-2-yl)-9-(2-ethylhexyl)-9H-purin-6-amine (**10**) *and 8,8′-(5,5′-(Benzo[c][1,2,5]-thiadiazole-4,7-diyl)bis(thiophene-5,2-diyl))bis(9-(2-ethylhexyl)-9H-purin-6-amine)* (**1a**). In a dry round-bottom flask under an inert atmosphere, **17** (0.052 g, 0.13 mmol), K_2CO_3 (0.32 g, 2.4 mmol), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (0.018 g, 0.027 mmol), and Aliquat 336 (2 drops) were dissolved in a degassed solution of **7** (0.12 g, 0.29 mmol) in toluene (6 mL). Then, degassed water (2 mL) was added and the reaction vessel was heated to 85 °C for 18 h. The solvent was removed under reduced pressure, and the residue was dissolved in EtOAc (25 mL), washed with water (3 × 15 mL), and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography with gradient elution ($MeOH:CH_2Cl_2$ 1:99 to 4:95). The mixture of **1a** and **10** was further purified by precipitation from hexanes.

10. Yellow solid (0.010 g, 30%): mp 185 °C (dec); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.21 (d, J = 4.2 Hz, 1H), 8.01−7.94 (m, 3H), 7.70−7.65 (m, 2H), 5.59 (s, 2H), 4.43 (d, J = 7.8 Hz, 2H), 2.08−2.02 (m, 1H), 1.28−1.25 (m, 8H), 0.89−0.81 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6, 154.6, 152.3, 152.1, 151.9, 151.9, 145.8, 142.4, 132.9, 129.7, 128.8, 128.3, 126.7, 126.0, 121.2, 48.0, 39.2, 29.8, 28.4, 23.8, 23.1, 14.1, 10.6; HRMS (ESI) calcd for $C_{23}H_{26}N_7S_2$ $[M + H]^+$: 464.1691, found: 464.1707.

1a. Mixture of stereoisomers as a red solid (0.045 g, 42%): ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.34 (s, 2H), 8.29 (d, J = 4.0 Hz, 2H), 8.18 (s, 2H), 7.87 (d, J = 4 Hz, 2H), 7.37 (s, 4H), 4.23 (d, J = 7.5 Hz, 4H), 1.94−1.90 (m, 2H), 1.23−1.20 (m, 16H), 0.81−0.72 (m, 12H); ^{13}C NMR (125 MHz, DMSO-d_6, gHMBC): δ 156.3, 153.4, 152.7, 152.5, 144.6, 141.2, 134.9, 129.0, 128.8, 127.0, 125.7, 119.5, 47.8, 39.2, 30.6, 28.5, 24.2, 23.0, 14.2, 11.0; HRMS (APCI) calcd for $C_{40}H_{47}N_{12}S_3$ $[M + H]^+$: 791.3209, found: 791.3184.

8,8′-([2,2′:5′,2″-Terthiophene]-5,5″-diyl)bis(9-(2-ethylhexyl)-9H-purin-6-amine) (**2a**). In a dry round-bottom flask under an inert atmosphere, **7** (0.18 g, 0.45 mmol), **9** (0.070 g, 0.22 mmol), K_2CO_3 (0.50 g, 3.6 mmol), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (0.03 g, 0.04 mmol), and Aliquat 336 (2 drops) were dissolved in degassed toluene (6 mL), followed by addition of degassed water (2 mL). The reaction vessel was heated to 80 °C and stirred for 18 h, filtered, and washed with CH_2Cl_2 (15 mL). The product was further purified by precipitation from hexanes to afford the orange product as a mixture of stereoisomers (0.06 g, 40%): ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.17 (s, 2 H), 7.70 (d, J = 3.9 Hz, 2H), 7.53 (d, J = 3.9 Hz, 2H), 7.33 (s, 4H), 7.49 (s, 2H), 4.37 (d, J = 7.5 Hz, 4H), 1.88−1.86 (m, 2H), 1.21−1.10 (m, 16H), 0.81−0.72 (m, 12H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 155.5, 152.7, 151.7, 143.2, 138.0, 135.3, 131.3, 128.7, 126.3, 125.4, 118.5, 46.7, 38.2, 29.6, 27.6, 23.3, 22.3, 13.8, 10.4; HRMS (APCI) calcd for $C_{38}H_{46}N_{10}S_3$ $[M + H]^+$: 739.3142, found: 739.3144.

Synthesis of Guanine-Terminated Oligomers. *(±)-6-Chloro-9-(2-ethylhexyl)-9H-purin-2-amine* (**12**). K_2CO_3 (2.45 g, 17.7 mmol) was added to a solution of 6-chloro-9*H*-purin-2-amine **11** (1.0 g, 5.9 mmol) in dry DMF (100 mL), then stirred at rt for 1 h. Racemic 2-ethylhexyl bromide was then added, and the solution was allowed to stir for 16 h. The solvent was removed under reduced pressure, and the resulting crude mixture was purified by silica gel column chromatography with gradient elution (EtOAc:hexanes 30:70 to 50:50) to yield a white solid (0.92 g, 56%): mp 107 °C (dec); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.71 (s, 1H), 5.32 (s, 2H), 3.95 (d, J = 7.0 Hz, 2H), 1.88−1.86 (m, 1H), 1.28−1.24 (m, 8H), 0.90−0.83 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 154.3, 151.2, 142.9, 125.2, 47.3, 39.6, 30.4, 28.5, 23.7, 23.0, 14.1, 10.5; HRMS (ESI) calcd for $C_{13}H_{21}ClN_5$ $[M + H]^+$: 282.1485, found: 282.1472.

(±)-2-Amino-9-(2-ethylhexyl)-1,9-dihydro-6H-purin-6-one (**13**). 6-Chloro-9*H*-purin-2-amine **11** (0.30 g, 1.1 mmol) was dissolved in a 3 M HCl solution (10 mL) and heated to reflux for 5 h. The reaction mixture was then cooled to rt, and neutralized with 1 M NaOH solution. The precipitate formed was filtered and dried under vacuum (0.27 g, 98%): mp 292 °C (dec); ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.66 (s, 1H), 7.75 (s, 1H), 6.49 (s, 2H), 3.83 (d, J = 7 Hz, 2H), 1.85 (sep, J = 6 Hz, 1H), 1.25−1.16 (m, 8H), 0.84−0.81 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.5, 153.2, 151.2, 137.3, 116.3, 46.0, 38.6, 29.6, 27.5, 23.1, 22.0, 13.3, 9.9; HRMS (ESI) calcd for $C_{13}H_{21}N_5O$ $[M + H]^+$: 264.1819, found: 264.1816.

(±)-2-Amino-8-bromo-9-(2-ethylhexyl)-1,9-dihydro-6H-purin-6-one (**14**). NBS (0.27 g, 1.5 mmol) was added portionwise to a slurry of (±)-2-amino-9-(2-ethylhexyl)-1,9-dihydro-6*H*-purin-6-one **13** (0.26 g, 1.0 mmol) in acetonitrile (15 mL) and stirred overnight at rt. The solvent was removed under reduced pressure. The crude solid was washed with DCM to afford the product as a pale yellow solid (0.26 g, 75%): mp 300 °C (dec); ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.71 (s, 1H), 6.58 (s, 2H), 3.80 (d, J = 12.5 Hz, 2H), 1.96−1.87 (m, 1H), 1.29−1.17 (m, 8H), 0.87−0.79 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 155.5, 153.8, 152.8, 120.8, 116.7,47.3, 38.4, 29.7, 27.8, 23.3, 22.4, 13.7, 10.5; HRMS (ESI) calcd for $C_{13}H_{20}BrN_5O$ $[M + H]^+$: 342.0924, found: 342.0886.

(±)-2-Amino-9-(2-ethylhexyl)-8-(thiophen-2-yl)-1,9-dihydro-6H-purin-6-one (**15**). (±)-2-Amino-8-bromo-9-(2-ethylhexyl)-1,9-dihydro-6*H*-purin-6-one **14** (0.30 g, 0.88 mmol), 2-(tributylstannyl)-thiophene (1.4 mL, 4.4 mmol), $Pd(PPh_3)_4$ (0.20g, 0.17 mmol), and Ph_3Bi (0.019 g, 0.04 mmol) were dissolved in dry and degassed xylene (20 mL) and heated to reflux overnight. The reaction mixture was cooled to rt, and concentrated under reduced pressure. The crude solid was washed with DCM to afford the title product as a white solid (0.20, 66%): mp > 350 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.79 (s, 1H), 7.74 (d, J = 5.5 Hz, 1H), 7.58 (d, J = 3.5 Hz, 1H), 7.21 (dd, J = 4, 5 Hz, 1H), 6.64 (b, 1H), 4.14 (d, J = 8 Hz, 2H), 1.77−1.69 (m, 1H), 1.20−1.01 (m, 8H), 0.77−0.73 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.0, 153.7, 152.9, 140.6, 131.5, 128.6, 128.0, 127.2, 115.0, 46.5, 37.9, 29.5, 27.5, 23.2, 22.3, 13.7, 10.3; HRMS (ESI) calcd for $C_{17}H_{23}N_5OS$ $[M + H]^+$: 346.1696, found: 346.1706.

(±)-6-(Benzyloxy)-9-(2-ethylhexyl)-9H-purin-2-amine (**18**). A dry round-bottom flask equipped with a condenser under an inert argon atmosphere was charged with **12** (0.50 g, 1.8 mmol), K_2CO_3 (0.25 g, 1.8 mmol), 1,4-diazabicyclo[2.2.2]octane (0.020 g, 0.18 mmol), and benzyl alcohol (3 mL). The reaction was heated to 80 °C and stirred for 16 h and then cooled to rt. The solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography with a gradient elution (EtOAc:hexanes 20:80 to 40:60) to yield a white solid (0.53 g, 84%): mp 102−104 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (s, 1H), 7.52−7.50 (m, 2H), 7.37−7.28 (m, 3H), 5.56 (s, 2H), 4.81 (bs, 2H), 3.94 (d, J = 7.0 Hz, 2H), 1.89 (sep, J = 6.5 Hz, 1H), 1.28−1.27 (m, 8H), 0.92−0.86 (m, 6H); ^{13}C

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NMR (125 MHz, CDCl3): δ 161.1, 159.2, 154.7, 140.0, 136.7, 128.5, 128.4, 128.1, 115.7, 68.1, 47.1, 39.7, 30.4, 28.6, 23.8, 23.1, 14.2, 10.6; HRMS (ESI) calcd for $C_{20}H_{28}N_5O$ $[M + H]^+$: 354.2294, found: 354.2300.

*(±)-6-(Benzyloxy)-8-bromo-9-(2-ethylhexyl)-9H-purin-2-amine (**19**).* NBS (0.55 g, 3.1 mmol) was added portionwise to a solution of **18** (1.0 g, 2.8 mmol) and stirred at rt for 1.5 h. The reaction mixture was then poured into deionized water (20 mL), extracted with ethyl acetate (25 mL), washed with a solution of 5% $Na_2S_2O_4$ (15 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield **19** as a beige solid (1.04 g, 85%): mp 106−108 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.50−7.48 (m, 2H), 7.36−7.30 (m, 3H), 5.52 (s, 2H), 4.86 (s, 2H), 3.93 (d, *J* = 8.0 Hz, 2H), 2.00 (sep, *J* = 6.5 Hz, 1H), 1.32−1.26 (m, 8H), 0.91−0.85 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 159.0, 155.6, 136.4, 128.5, 128.5, 128.2, 126.1, 115.9, 68.3, 48.1, 39.0, 30.4, 28.5, 23.8, 23.1, 14.1, 10.7; HRMS (ESI) calcd for $C_{40}H_{52}Br_2N_{10}NaO_2$ $[M + Na]^+$: 887.2519, found: 887.2547.

*(±)-6-(Benzyloxy)-9-(2-ethylhexyl)-8-(thiophen-2-yl)-9H-purin-2-amine (**20**).* Compound **19** (0.08 g, 0.2 mmol), Ph_3Bi (0.03 g, 0.07 mmol), and $Pd(PPh_3)_4$ (0.04 g, 0.03 mmol) were dissolved in dry degassed xylenes (5 mL), along with 2-(tributylstannyl)thiophene (0.2 mL, 0.5 mmol). The reaction vessel was heated to reflux for 10 min. The solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc:hexanes 10:90 to 40:60) to yield the product as a white solid (0.07 g, 97%): mp 136−138 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53−7.51 (m, 3H), 7.44−7.43 (m, 1H), 7.36−7.33 (m, 2H), 7.31−7.28 (m, 1H), 7.13−7.11 (m, 1H), 5.59 (s, 2H), 4.86 (s, 2H), 4.21 (d, *J* = 7.5 Hz, 2H), 1.91−1.89 (m, 1H), 1.25−1.17 (m, 8H), 0.83−0.78 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.7, 158.9, 156.5, 144.6, 136.7, 132.6, 128.6, 128.4, 128.1, 127.9, 127.8, 127.6, 115.4, 68.2, 47.4, 38.9, 30.3, 28.3, 23.7, 23.0, 14.1, 10.6; HRMS (ESI) calcd for $C_{24}H_{30}N_5OS$ $[M + H]^+$: 436.2166, found: 436.2187.

*(±)-6-(Benzyloxy)-8-(5-bromothiophen-2-yl)-9-(2-ethylhexyl)-9H-purin-2-amine (**21**).* In a dry round-bottom flask under an inert atmosphere, **20** (0.12 g, 0.28 mmol) was dissolved in dry THF (3 mL). To this solution, glacial HOAc (2 mL) was added, and the contents of the reaction vessel were cooled to 0 °C in an ice−water bath. Next, NBS (0.050 g, 0.30 mmol) was added and the reaction was slowly warmed to rt over 1.5 h. The solvent was removed under reduced pressure to yield the crude product, which was subsequently diluted with EtOAc (50 mL) and washed with saturated NaCl solution (3 × 25 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered, and evaporated to yield **21** as beige solid (0.13 g, 93%): mp: 129−131 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53−7.51 (m, 2H), 7.37−7.30 (m, 3H), 7.24 (d, *J* = 4.0 Hz, 1H), 7.07 (d, *J* = 4.0 Hz, 1H), 5.58 (s, 2H), 4.85 (s, 2H), 4.16 (d, *J* = 7.5 Hz, 2H), 1.94−1.86 (m, 1H), 1.25−1.22 (m, 8H), 0.84−0.80 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.8, 159.0, 156.4, 143.4, 136.6, 134.5, 130.5, 128.6, 128.5, 128.1, 127.6, 115.4, 115.2, 68.3, 47.4, 38.9, 30.3, 28.3, 23.7, 23.0, 14.1, 10.6; HRMS (ESI) calcd for $C_{24}H_{29}BrN_5OS$ $[M + H]^+$: 516.1253, found: 516.1266.

*8,8′-(5,5′-(Benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(thiophene-5,2-diyl))bis(6-(benzyloxy)-9-(2-ethylhexyl)-9H-purin-2-amine) (**1b**).* In a dry round-bottom flask under an inert atmosphere, K_2CO_3 (0.24 g, 1.8 mmol), Aliquat 336 (2 drops), and $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (0.020 g, 0.020 mmol), **21** (0.050 g, 1.4 mmol), and **8** (0.11 g, 0.22 mmol) were dissolved in degassed toluene (6 mL), followed by addition of degassed water (2 mL). The reaction was then heated to 80 °C for 17 h. The reaction mixture was diluted with EtOAc (75 mL). The organic layer was separated from the aqueous phase and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure to yield a crude red product, which was then precipitated from a mixture of CH_2Cl_2 in hexanes to yield the red product as a mixture of stereoisomers (0.11 g, 97%): ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19(d, *J* = 4.0 Hz, 2H), 7.94 (s, 2H), 7.65 (d, *J* = 4.5 Hz, 2H), 7.56−7.52 (m, 4 H), 7.39−7.32 (m, 6 H), 5.62 (s, 4H), 4.86 (s, 4H), 4.31 (d, *J* = 7.5 Hz, 4H), 2.03−2.00 (m, 2H), 1.32−1.25 (m, 16H), 0.89−0.81 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.8, 159.0, 156.6, 152.6, 144.4, 141.3, 136.7, 133.9, 128.7, 128.5, 128.3, 128.2, 128.1, 126.0, 125.9, 115.7, 68.3, 47.6, 39.1, 30.4, 28.4, 23.8, 23.1, 14.2, 10.7; HRMS (APCI) calcd for $C_{54}H_{59}N_{12}O_2S_3$ $[M + H]^+$: 1003.4046, found: 1003.4026.

*8,8′-(5,5′-(Benzo[c][1,2,5]thiadiazole-4,7-diyl)bis(thiophene-5,2-diyl))bis(2-amino-9-(2-ethylhexyl)-1H-purin-6(9H)-one) (**1c**).* In a dry round-bottom flask under an inert atmosphere, a solution of pentamethylbenzene (0.050 g, 0.32 mmol) and **1b** (0.080 g, 0.080 mmol) in dry degassed CH_2Cl_2 (75 mL) was cooled to −78 °C and then a 1.0 M solution of BCl_3 in CH_2Cl_2 (0.53 mL, 0.54 mmol) was added slowly over 15 min. The solution was stirred at −78 °C for 40 min, followed by the addition of methanol (25 mL) to quench the reaction. The solvent was removed under reduced pressure to yield a crude purple solid **1c** that was subsequently washed with DCM to remove impurities and afford the product as a mixture of stereoisomers (0.06 g, 95%): ^{1}H NMR (500 MHz, DMSO-d_6): δ 10. 85 (s, 2 H), 8.24 (s, 2 H), 8.22 (d, *J* = 3.5 Hz, 2H), 7.68 (d, *J* = 4.0 Hz, 2H), 6.72 (s, 4H), 4.23 (d, *J* = 7.5 Hz, 4H), 1.88−1.86 (m, 2H), 1.23−1.20 (m, 16H), 0.82−0.75 (m, 12H); ^{13}C NMR (125 MHz, DMSO-d_6): δ 156.1, 153.9, 153.2, 152.0, 140.8, 139.5, 135.5, 133.8, 128.5, 126.7, 126.3, 125.2, 47.0, 38.6, 30.1, 28.1, 23.7, 22.8, 14.2, 10.9; HRMS (APCI) calcd for $C_{40}H_{46}N_{12}NaO_2S_3$ $[M + H]^+$: 845.2927, found: 845.2883.

*8,8′-([2,2′:5′,2″-Terthiophene]-5,5″-diyl)bis(6-(benzyloxy)-9-(2-ethylhexyl)-9H-purin-2-amine) (**2b**).* In a dry round-bottom flask under an inert atmosphere, a solution of **21** (0.10 g, 0.20 mmol), **9** (0.030 g, 0.10 mmol), K_2CO_3 (0.22 g, 1.6 mmol), $Pd(dppf)Cl_2{\cdot}CH_2Cl_2$ (0.020 g, 0.020 mmol), and Aliquat 336 (2 drops) in degassed toluene (6 mL), and degassed water (2 mL) was heated to 80 °C for 18 h. The solvent was removed under reduced pressure. The crude solid was dissolved in CH_2Cl_2, washed with water, and dried over anhydrous Na_2SO_4. The crude product was purified by silica gel column chromatography (EtOAc:hexanes 10:90 to 40:60) to afford **2b** as an orange mixture of stereoisomers (0.05 g, 49%): ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (d, *J* = 6.5 Hz, 2H), 7.43 (d, *J* = 4.0 Hz, 2H), 7.38−7.34 (m, 4H), 7.32−7.31 (m, 2H), 7.18 (d, *J* = 4.0 Hz, 4H), 7.16 (s, 2H), 5.59 (s, 4H), 4.87 (s, 4H), 4.23 (d, *J* = 7.5 Hz, 4H), 1.97 (sep, *J* = 6.5 Hz, 2H), 1.29−1.26 (m, 16H), 0.87−0.81 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.7, 158.9, 156.5, 144.0, 139.1, 136.7, 136.2, 131.7, 128.6, 128.5, 128.1, 128.0, 125.4, 124.2, 115.5, 68.2, 47.5, 39.9, 30.3, 28.4, 23.7, 23.1, 14.1, 10.6; HRMS (APCI) calcd for $C_{52}H_{58}N_{10}O_2S_3$ $[M + H]^+$: 951.3979, found: 951.3987.

*8,8′-([2,2′:5′,2″-Terthiophene]-5,5″-diyl)bis(2-amino-9-(2-ethylhexyl)-1H-purin-6(9H)-one) (**2c**).* In a dry round-bottom flask under an inert atmosphere, a solution of pentamethylbenzene (0.030 g, 0.18 mmol) and **2b** (0.043 g, 0.045 mmol) in dry degassed CH_2Cl_2 (15 mL) was cooled to −78 °C and then a 1.0 M solution of BCl_3 in CH_2Cl_2 (0.27 mL, 0.27 mmol) was added slowly over 15 min. The solution was stirred at −78 °C for 2 h, and then quenched with methanol (25 mL). The solvent was removed under reduced pressure to yield a crude red solid that was subsequently washed with chloroform to remove impurities (0.03 g, 88%): ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.85 (s, 2H), 7.56 (d, *J* = 4.0 Hz, 2H), 7.50−7.44 (m, 4H), 6.70 (s, 4H), 4.17 (d, *J* = 7.5 Hz, 4H), 1.83−1.81 (m, 2H), 1.23−1.16 (m, 16H), 0.80−0.76 (m, 12H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 155.2, 154.3, 152.4, 139.6, 138.3, 135.1, 129.5, 128.4, 126.5, 125.3, 113.4, 46.8, 37.9, 29.4, 27.5, 23.1, 22.3, 13.8, 10.3; HRMS (APCI) calcd for $C_{38}H_{46}N_{10}O_2S_3$ $[M + H]^+$: 771.3040, found: 771.3007.

Synthesis of Uracil-Terminated Oligomers. *(±)-1-(2-Ethylhexyl)pyrimidine-2,4(1H,3H)-dione (**23**).* A suspension of uracil **22** (2.00 g, 17.8 mmol), and anhydrous K_2CO_3 (2.70 g, 19.6 mmol) in DMSO (20 mL) was stirred for 15−20 min. *rac*-2-Ethylhexyl bromide (4.80 mL, 26.7 mmol) was added, and the reaction mixture was stirred for 20 h at 40 °C. The suspension was diluted with EtOAc, washed with H_2O (20 mL × 2) and brine (20 mL × 2), and dried over Na_2SO_4. The organic layer was concentrated under reduced pressure and poured into cold hexane. The resulting precipitate was filtered and washed with hexane to afford compound **23** (0.8 g, 29%) as a white solid: mp 80−82 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.80 (s, 1H), 7.10 (d, *J* = 7.8 Hz, 1H), 5.68 (d, *J* = 7.8 Hz, 1H), 3.61 (d, *J* = 7.2 Hz,

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2H), 1.77−1.72 (m, 1H), 1.33−1.28 (m, 8H), 0.93−0.87 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.1, 151.3, 145.0, 101.9, 52.4, 38.9, 30.2, 28.5, 23.5, 23.0, 14.1, 10.5; HRMS (ESI) calcd for $C_{12}H_{20}N_2O_2$ [M + Na]$^+$: 247.1417, found: 247.1426.

(±)-5-Bromo-1-(2-Ethylhexyl)pyrimidine-2,4(1H,3H)-dione (**24**). To a solution of **23** (0.50 g, 2.4 mmol) in dry DMF (20 mL), NBS (0.50 g, 2.6 mmol) was added. The reaction mixture was stirred for 15 min at rt. The solvent was removed under reduced pressure, and the resulting suspension was poured into cold hexanes. The resulting precipitate was filtered and washed with water to afford compound **24** as a white solid (0.7 g, 60%): mp 156−158 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.43 (s, 1H), 7.45 (s, 1H), 3.31 (d, *J* = 7.2 Hz, 2H), 1.75−1.71 (m, 1H), 1.32−1.28 (m, 8H), 0.93−0.88 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.7, 155.2, 150.6, 144.3, 96.2, 52.8, 39.0, 30.1, 28.5, 23.0, 14.1, 10.5; HRMS (ESI) calcd for $C_{12}H_{19}BrN_2O_2$ [M + H]$^+$: 303.0703/305.0683, found: 303.0707/305.0685.

(±)-1-(2-Ethylhexyl)-5-(thiophen-2-yl)pyrimidine-2,4(1H,3H)-dione (**25**). 2-Tributylstannylthiophene (1.70 mL, 5.30 mmol) was added to a solution of **24** (0.40 g, 1.3 mmol) and $Pd(PPh_3)_4$ (0.10 g, 0.10 mmol) in dry and degassed 1,4-dioxane (30 mL), then stirred at 120 °C overnight. The reaction mixture was cooled to rt, then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (EtOAc:hexanes 20:80) to afford the title compound **25** as a white solid (0.30 g, 63%): mp 88−90 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.85 (s, 1H), 7.46 (s, 1H), 7.42 (dd, *J* = 3.5, 1 Hz, 1H), 7.30 (dd, *J* = 5, 1 Hz, 1H), 7.10 (dd, *J* = 5.5, 4 Hz, 1H), 3.71 (d, *J* = 7.5 Hz, 2H), 1.82−1.80 (m, 1H), 1.40−1.29 (m, 8H), 0.95−0.89 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.8, 150.4, 139.9, 133.5, 127.2, 125.4, 124.4, 109.7, 52.7, 38.9, 30.1, 28.5, 23.5, 23.1, 14.1, 10.5; HRMS (ESI) calcd for $C_{16}H_{22}N_2O_2S$ [M + Na]$^+$: 329.1294, found: 329.1288.

(±)-5-(4,5-Dibromothiophen-2-yl)-1-(2-ethylhexyl)pyrimidine-2,4(1H,3H)-dione (**26′**). NBS (0.15 g, 0.83 mmol) was added portionwise to a solution of (±)-1-(2-ethylhexyl)-5-(thiophen-2-yl)pyrimidine-2,4(1*H*,3*H*)-dione **25** (0.25g, 0.76 mmol) in THF (10 mL) and AcOH (10 mL) at 0 °C. The reaction mixture was stirred for 30 min, then warmed to rt, poured in water, and extracted with DCM (3 × 25 mL). The organic layer was dried over Na_2SO_4, and concentrated under reduced pressure. The crude solid was purified by column chromatography on silica gel (EtOAc:hexanes 20:80) to afford the product as a white solid (0.17 g, 45%): mp 150−152 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.38 (s, 1H), 7.93 (s, 1H), 6.98 (s, 1H), 3.71 (d, *J* = 7.5 Hz, 2H), 1.82 (sep, *J* = 6 Hz, 1H), 1.43−1.25 (m, 8H), 0.94−0.88 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.8, 150.1, 144.2, 132.3, 129.5, 114.4, 107.3, 106.9, 53.1, 39.1, 30.3, 28.6, 23.5, 23.1, 14.2, 10.6; HRMS (ESI) calcd for $C_{16}H_{20}Br_2N_2O_2S$ [M + Na]$^+$: 486.9484, found: 486.9486.

5,5′-(Benzo[c][1,2,5]thiadiazole-4,7-diylbis(thiophene-5,2-diyl))-bis(1-(2-ethylhexyl)pyrimidine-2,4(1H,3H)-dione) (**1d**). Compound **24** (0.45 g, 1.5 mmol) and $PdCl_2(PPh3)_2$ (0.11 g, 0.15 mmol) were mixed in dry and degassed 1,4-dioxane (8 mL), **17** (0.10 g, 0.83 mmol) was added to the solution, and it was stirred at 100 °C overnight. The solvent was removed under reduced pressure, and the crude was purified by silica gel column chromatography (EtOAc:hexanes 80:20) to afford the target compound **1d** as a dark red solid (mixture of stereoisomers) (0.28g, 50%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.73 (s, 1H), 8.47 (s, 1H), 8.13 (d, *J* = 6.5 Hz, 1H), 8.06 (s, 1H), 7.66 (d, *J* = 6.5 Hz, 1H), 3.73 (d, *J* = 11 Hz, 2H), 1.89−1.78 (m, 1H), 1.27−1.22 (m, 8H), 0.90−0.83 (m, 6H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 161.6, 151.7, 149.9, 141.6, 137.6, 135.9, 126.8, 125.3, 124.8, 123.3, 107.3, 51.6, 37.7, 29.3, 27.8, 22.8, 22.4, 13.9, 10.3; HRMS (ESI) calcd for $C_{38}H_{44}N_6O_4S_3$ [M + H]$^+$: 745.2659, found: 745.2642.

5,5′-([2,2′:5′,2″-Terthiophene]-5,5″-diyl)bis(1-(2-ethylhexyl)-pyrimidine-2,4(1H,3H)-dione) (**2d**). Compound **24** (0.1 g, 0.3 mmol) and $PdCl_2(PPh_3)_2$ (0.02 g, 0.03 mmol) were mixed in dry and degassed 1,4-dioxane (8 mL), **27** (0.1 g, 2.0 mmol) was added to the solution, and it was stirred at 100 °C overnight. The solvent was removed under reduced pressure, and the crude was purified by silica gel column chromatography (EtOAc:hexanes 80:20) to afford the target compound **2d** (mixture of stereoisomers) as a dark orange solid (0.08g, 70%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.47 (s, 1H), 7.47 (s, 1H), 7.33 (d, *J* = 4 Hz, 1H), 7.11 (d, *J* = 3.5 Hz, 2H), 3.72 (d, *J* = 6.5 Hz, 2H), 1.83−1.81 (m, 1H), 1.41−1.21 (m, 8H), 0.96 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 161.2, 149.8, 139.5, 137.1, 136.2, 132.4, 125.0, 124.6, 123.7, 109.5, 52.9, 38.1, 30.2, 28.5, 23.6, 23.1, 14.2, 10.6; HRMS (ESI) calcd for $C_{36}H_{44}N_4O_4S_3$ [M + H]$^+$: 693.2597, found: 693.2606.

Attempted Synthesis of Cytosine-Terminated Oligomers. *(±)-4-Amino-1-(2-ethylhexyl)pyrimidin-2(1H)-one* (**29**). $(Bu)_4NOH$ (18.0 mL, 72.0 mmol) was added to a suspension of cytosine **28** (2.00 g, 18.0 mmol) in DMF (200 mL), followed by dropwise addition of 2-ethylhexyl bromide (6.40 mL, 36.0 mmol) within 10 min. The mixture was stirred at rt overnight, then concentrated under reduced pressure, and precipitated from hexane. The resulting precipitate was filtered and washed with water to afford the product **29** (2.30 g, 57%) as a white solid: mp 201−203 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50 (d, *J* = 6.9, 1H), 6.93 (bs, 2H), 5.61 (d, *J* = 7.2 Hz, 1H), 3.51 (d, *J* = 7.2 Hz, 2H), 1.73−1.69 (m, 1H), 1.25−1.16 (m, 8H), 0.87−0.79 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 164.7, 155.9, 146.4, 92.7, 52.3, 37.7, 29.6, 28.0, 23.0, 22.4, 13.9, 10.3; HRMS (ESI) calcd for $C_{12}H_{21}N_3O$ [M + H]$^+$: 224.1757, found: 224.1767.

(±)-4-Amino-5-bromo-1-(2-ethylhexyl)pyrimidin-2(1H)-one (**30**). NBS (0.90 g, 5.0 mmol) was added to a solution of **29** (1.00 g, 4.50 mmol) in dry DMF (100 mL). The reaction mixture was then stirred for 2 h at rt. The solvent was concentrated under vacuum. The crude product was dissolved in DCM, washed with 5% $Na_2S_2O_3$ (20 mL) and brine (20 mL), and then dried over Na_2SO_4. The organic layer was concentrated under reduced pressure and purified by column chromatography on silica gel (MeOH:DCM 5:95) to afford the product **30** as a pale yellow solid (0.60 g, 45%): mp 131−133 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.64 (s, 1H), 6.82 (s, 1H), 3.56 (d, *J* = 7.5 Hz, 2H), 1.75−1.71 (m, 1H), 1.25−1.18 (m, 8H), 0.86−0.80 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 162.6, 155.5, 145.8, 86.7, 54.1, 38.6, 30.1, 28.5, 23.5, 23.1, 14.1, 10.5; HRMS (ESI) calcd for $C_{12}H_{20}BrN_3O$ [M + H]$^+$: 302.0863/304.0843, found: 302.0866/304.0852.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Solubility studies, TGA, UV−vis spectra (and Beer−Lambert plots) and details of photophysical measurements, electrochemistry (CV and DPV) details and data, computational details (including the coordinates of optimized structures), and copies of ^{1}H and ^{13}C NMR spectra. 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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