Fluorescent Thiophene-based Materials and Their Outlook for Emissive Applications

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FEATURE ARTICLE

Fluorescent Thiophene-based Materials and Their Outlook for Emissive Applications

Seth C. Rasmussen*[a], Sean J. Evenson[a], and Casey B. McCausland[a]

Although thiophene-based materials are among the most widely studied conjugated materials for a number of technological applications, most discussions of emissive conjugated materials have focused on other systems, primarily due to the lower emission quantum yields of thiophene-based systems. Over the last decade, however, this has begun to change with the development of new highly emissive thiophene-based materials. In this review, we provide an overview of fluorescent thiophene-based materials and their applications, highlighting in particular the various methods employed to achieve highly emissive materials, as well as a variety of reported applications including fluorescent biomarkers and organic light emitting diodes.

1. Introduction

Although the production and study of conjugated organic polymers (Fig. 1) dates back to at least the beginning of the 20th century, it was the discovery of their conductive nature that lead to more extensive research beginning in the early 1960s.[1] Since that time, conjugated polymers have grown to receive considerable fundamental and technological interest due to their combination of the electronic and optical properties of classical inorganic semiconductors with many of the desirable properties of typical organic plastics, most notably mechanical flexibility and low production costs.[1-3] Advances in the technological applications of these materials have resulted in the current growth of the field of organic electronics, with considerable effort focused on the development of applications such as sensors, electrochromic devices, field-effect transistors (FETs), organic photovoltaics (OPVs), and organic light-emitting
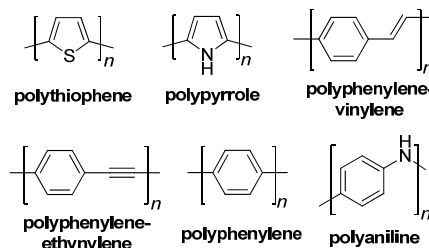

Fig. 1 Commonly studied parent conjugated polymers

diodes (OLEDs).[2-9] Of particular interest is the exciting promise of flexible electronics, a realistic goal for the near future that is made possible by the flexible, plastic nature of the organic materials used as the active layers in these electronic devices.[9]

Of the commonly studied materials shown in Fig. 1, poly-

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and study of conjugated systems, with particular interest in developing deeper understanding of their structure-function relationships.

Sean Evenson was born in west central Minnesota and attended Gustavus Adolphus College where he received a B.A. in Chemistry in 2006. In the fall of 2011, he graduated with his Ph.D. under the supervision of Prof. Seth Rasmussen at NDSU. His Ph.D. research focused on the synthesis and characterization of organic semiconducting materials derived from first and second generation N-functionalized dithieno[3,2-b:2',3'-d]pyrrole-based systems, as well as their applications in

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thiophenes and thiophene-based materials are thought to be some of the most versatile conjugated materials due to their combination of environmental stability and ease of synthetic modification.[4,5] As a result, thiophene-based materials typically exhibit the greatest amount of structural diversity and are typically the most commonly studied materials for applications such as OPVs. Their use in emissive applications, however, falls far behind those of the various phenylene materials included in Fig. 1 as a result of limited fluorescent quantum yields in both solution and the solid state.[5-8] The limited emission in these materials is typically attributed to the inclusion of the heavy sulphur atom, as well as the efficient solid-state packing characteristic of thiophene-based materials.[5-8]

Regardless of this limitation, thiophene-based materials still provide a number of characteristics that have made them popular systems for technological applications. In addition to the stability and synthetic diversity already discussed, these include controllable colour tuning of the absorption and emission,[2-8] good charge mobility,[3] and the ability to produce materials with lower band gaps than the other commonly studied materials given in Fig. 1.[10] As such, thiophene-based materials are still of significant interest for emissive applications and this interest has increased as a result of various approaches for overcoming the commonly reduced fluorescence efficiencies, as well as new applications such as fluorescent biomarkers. Therefore, this review will strive to give the reader a good overview of the structure-function relationships relating to emission in these materials, while also presenting the recent advancements in thiophene-based materials and their applications.

2. Basic photophysics of thiophene-based systems

The nature of the absorption processes in the majority of thiophene-based systems are simple $\pi \rightarrow \pi^*$ transitions resulting in the population of a singlet excited state (S_1, Fig. 2).[11] Sulfur-based $n \rightarrow \pi^*$ transitions are theoretically possible, but the molecular orbital (MO) comprising the sulphur lone pair lies at energies below multiple π-based MOs and such transitions have not yet been observed for thiophenes.[12] The energies of these transitions are dependent on a number of factors, the most basic of which are the overall length of the conjugation path and the molecule's planarity.[10,11,13,14] In solution, these materials exhibit a fairly structureless absorption thought to be the result of torsional rotational around the interannular bonds of the material

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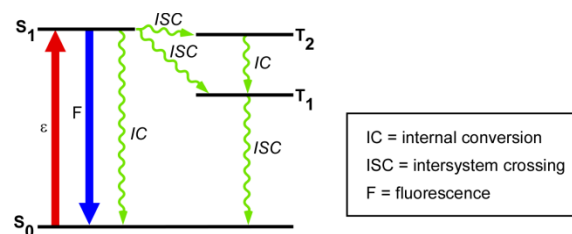
Casey McCausland

Fig. 2 Simplified Jablonski diagram showing basic photophysical processes

backbone.[15,16] This backbone is generally believed to adopt a twisted conformation,[5,14,16-18] with the extent of coiling being somewhat solvent and temperature dependent.

At low temperature (77-80 K), the absorption spectra show increased structure and a considerable red shift in the absorption maxima in comparison to those at room temperature.[5,11,17] Much smaller red shifts, however, are observed for the absorption onsets.[17] This temperature dependence is typically attributed to increased planarity of the ground state with reduced temperature, resulting in enhanced conjugation.[11,17]

In contrast to the absorption spectra, the solution fluorescence spectra tend to exhibit structured bands with vibrational spacing of about 1500 cm^{-1}, attributed to C=C stretching. These spectral characteristics are typically attributed to a narrow distribution of excited-state molecular geometries, characterized by a rigid planar quinoid-like structure (Fig. 3) for the excited singlet state, S_1, in comparison to the twisted aromatic structure of the ground state.[5,11,14-19] As the excited state already consists of a planar structure, the fluorescence does not exhibit the temperature effects observed for the absorption spectra.[17] The quinoid-like structure attributed to S_1 results in the absence of any significant coupling between the modes of S_1 and the twisted ground state, resulting in the absence of meaningful deactivation of S_1 via internal conversion (IC).[18]

Thiophene-based chromophores tend to exhibit weak fluorescence with low fluorescent quantum yields (Φ_F), thought to be due to significant spin-orbit coupling as a result of sulphur. The magnitude of sulphur-mediated spin-orbit coupling has been attributed to various factors, including the classical heavy atom effect,[5-7,17] contributions of sulphur 3d orbitals to the $\pi\pi^*$ wavefunction,[20] and coupling mediated by charge transfer mixing.[17] The spin-orbit coupling factor (ζ) is related to the spin-orbit interaction of an electron in a specific open-shell orbit of the heavy atom with its core in a specific electronic configuration.[21] For sulphur, the reported ζ values are considered to be relatively large; 184-186 cm^{-1} for 3p electrons[19,20] and 363-365 cm^{-1} for 3d electrons.[17,21]

The strong spin-orbit coupling of sulphur ultimately results in efficient intersystem crossing (ISC) and high triplet quantum yields (Φ_T) for thiophene-based materials (Φ_T = 0.94-0.99 for bithiophene).[17,19] The direct transition from the triplet excited state (T_1) to the ground state (S_0), however, is either dipole forbidden or weakly allowed.[15] This fact, combined with highly efficient non-radiative processes between T_1 and S_0, then leads to relaxation without emission.[5,17] For oligothiophenes, nonradiative deactivation is believed to be due to low frequency, inter-annular torsional vibrations, which are expected to be dominant in the twisted form of the solvated materials.[5,14,17,22,23]
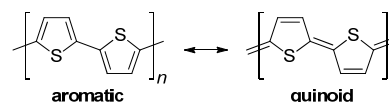

Fig. 3 Aromatic vs. quinoid resonance forms of oligo- and poly-thiophenes

Increasing the length of oligothiophenes, however, has revealed that both k_{ISC} and the triplet quantum yields decrease with conjugation length and the corresponding Φ_F thus increases.[15-17] This effect levels off after about five thiophene rings and the overall trend has been explained by measurement of the second triplet excited states (T_2) of oligothiophenes, which shows that the S_1 and T_2 states of bithiophene are at almost equal energies. This suggests the possibility of strongly mixed states, leading to an extremely high rate of intersystem crossing from S_1 to T_2 (Fig. 2).[19] As the oligomer size is increased, $\Delta E(S_1\text{-}T_1)$ decreases,[17] while the experimental energy position of T_2 becomes progressively higher than the S_1 band edge. As such, mixing of the singlet and triplet vibronic states still allows ISC, but with decreased S_1-T_2 coupling.[19] Thus for at least the lower oligomers, it is believed that nonradiative deactivation of the S_1 excited state occurs via ISC to higher triplet states, followed by IC to T_1, and then relaxation back to the ground state.[5,19] For polythiophenes, studies have shown that ISC via higher states is not competitive with ISC from S_1 to T_1.[24]

In the solid state, thiophene-based materials typically exhibit a red shift in absorbance,[15] typically ascribed to increased planarity of the conjugated backbone coupled with enhanced intermolecular interactions, such as π–π stacking, resulting in further electron delocalization.[25] Similar red shifts in fluorescence are also observed, although often to a lesser degree than that exhibited in the absorption due to the limited contribution from planarization of the backbone.[5] In addition, thin films with significant intermolecular interactions typically result in Φ_F values that are orders of magnitude lower than in solution (10-10^3 times lower for pure thiophene systems).[5-7,15,17] The reduced extent of emission is thought to be due to additional nonradiative mechanisms in the solid state in comparison to solution.[5,11,14,15] Possible contributions include interchain processes (e.g. formation of either excimers or exciton bands) as a result of cofacial packing of the planar backbones, which result in increased mobility and longer radiative lifetimes.[5-7,15,25] As a consequence, nonradiative quenching dominates the excited state decay in the solid state.[14,15] It has been proposed that a contributing factor could also be enhanced ISC in the solid-state due to a higher local concentration of sulphur in the surrounding thin film.[15] In addition, quenching of excitons is also possible via extrinsic or conformational defects.[14,15,26]

3. Simple thiophene materials

The most simple examples of thiophene-based materials are the α,α'-oligothiphenes (Fig. 4) and the corresponding parent polythiophene. As significant numbers of functionalized derivatives have also been reported, the discussion here will be limited to representative examples in order to highlight important structure-function relationships.
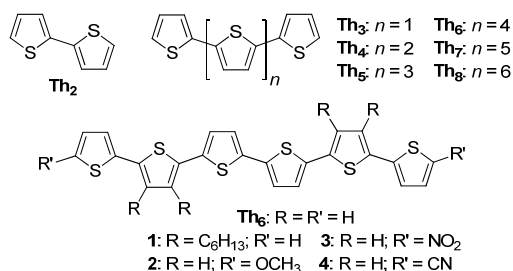
3.1 Oligothiophenes

The solution fluorescence of the simple unfunctionalized α,α'-oligothiophenes up to **Th$_6$** have been studied in detail and the corresponding data for the series is given in Table 1.[17] The unfunctionalized oligomers show that both absorption and emission shift to the red with increasing chain length. Additional trends include increases in Φ_F and the fluorescence lifetime with conjugation length, with a corresponding decrease in Φ_T.

Table 1 Solution photophysical data for representative α,α'-oligothiophenes[a]

Oligomer	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	τ_F (ns)	Φ_T	Ref
Th$_2$	303	362	0.017	0.046	0.94	17
Th$_3$	354	407,426	0.066	0.21	0.93	17
Th$_4$	392	437,478	0.18	0.49	0.67	17
Th$_5$	417	482,514	0.36	0.82	0.60	17
Th$_6$	436	502,537	0.41	1.0	0.60	17
1[b]	406	536	0.25	0.80		27
2[c]	442	528,562	0.14			28
3[c]	465	623	<0.025			28
4[d]	451	593	0.35	1.0		17

[a] Data collected in dioxane, unless otherwise specified. [b] In CHCl$_3$. [c] In CH$_2$Cl$_2$. [d] In DMSO.

The fluorescence properties of a variety of functionalized oligothiophenes have also been reported and some representative examples are included in Table 1.[8,17,27-29] The most common functionalization is simple alkyl chains, which result in a decrease in Φ_F. This effect can be due to the simple introduction of steric interactions that reduce backbone planarity, thus reducing the effective conjugation to result in decreased fluorescence.[22] In addition, alkyl groups add high-frequency modes that increase with the number of methylene units. These high-frequency modes result in a greater number of additional deactivation pathways via IC and a corresponding decrease in Φ_F.[30,31] Oligothiophenes have also been functionalized with a variety of electron-donating and accepting groups. In most cases, symmetrical functionalization (**2-4**) results in a decrease in fluorescence, although some increases in Φ_F have been reported for polar asymmetrical systems.[28,29]

The optical properties of the unfunctionalized α,α'-oligothiophenes in the solid state have also been studied and the collected data for the series **Th$_4$** to **Th$_8$** is given in Table 2. For these oligomers, the first absorption band consists of a broad continuum with a maximum that shifts to shorter wavelengths with decreasing film thickness. The band structure exhibits spacings of 1500-1750 cm^{-1}, with the lowest energy structural peak red-shifted by 1100 cm^{-1} in comparison to the analogous solution spectra, while the λ_{max} is blue-shifted from solution to the solid state.[32,33] The thin film emission is also red shifted in comparison to solution, coupled with a dramatic decrease in Φ_F as a result of the strong intermolecular inter-actions in the solid state.[33,34]

Fig. 4 α,α'-Oligothiophenes and representative sexithiophene derivatives.

Th$_3$: $n = 1$　**Th$_6$**: $n = 4$
Th$_4$: $n = 2$　**Th$_7$**: $n = 5$
Th$_5$: $n = 3$　**Th$_8$**: $n = 6$

Th$_6$: R = R' = H
1: R = C$_6$H$_{13}$; R' = H　**3**: R = H; R' = NO$_2$
2: R = H; R' = OCH$_3$　**4**: R = H; R' = CN

Table 2 Thin film data for representative α,α'-oligothiophenes

Oligomer	λ_{max}^{abs} (nm)[a]	λ_{max}^{em} (nm)	Φ_F	Ref
Th$_4$	407	520,559	0.02	32-34
Th$_5$	435	535,577	0.0013	32-34
Th$_6$	459	577,625	0.0018	32-34
Th$_7$	477	595,670	0.002	32-34
Th$_8$	486	614,681	0.001	32-34

[a] Maximum of the lowest absorption band independent of film thickness are estimated from HREEL spectra.

3.2 Polythiophenes

Due to the higher molecular weight of true polythiophenes, the insoluble nature of unfunctionalized materials prohibits solution studies and hinders significant thin film studies. As such, all reports of fluorescent polythiophenes have been limited to functionalized derivatives (Fig. 5). For the common polymers of monofunctionalized thiophenes, the asymmetric nature of the repeat unit allows for the possibility of three types of coupling: head-to-head (HH), head-to-tail (HT), and tail-to-tail (TT).[2-4,35] Uncontrolled polymerization leads to mixtures of these regioisomers, which result in undesirable steric interactions as illustrated in Figure 5. Such steric interactions are minimized with increasing HT content, resulting in increased conjugation and red shifts in both absorption and emission as shown by the data presented in Table 3.[22,35] The HT content also directly effects the strength of fluorescence, with higher regioregularity resulting in higher Φ_F values.[22,36]
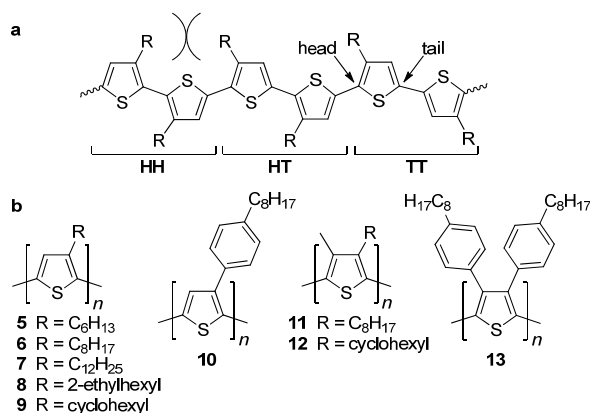

Fig. 5 Regioisomeric coupling (**a**) and representative polythiophenes (**b**)

Table 3 Photophysical data for representative polythiophenes

Polymer	%HT	Solution[a]			Thin film			Ref
		λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	
5	98	442			510	717		35
5	80	440	580	0.14	518	670	0.002	22
5	70	436			456	650		35
5	60	420	572	0.12	432	643	0.003	22
5	50	413	567	0.09	420	608	0.008	22
6	77	431	576	0.27	506	729	0.04	15
7	95	448[b]	580[b]	0.41[b]	536	735	0.01	36,37
7	60		575[b]	0.29[b]				36
8		425	569	0.26	464	593	0.09	15
9	77	425	571	0.27	405	574	0.09	15
10	91	463	587	0.18	555	764	0.03	15
11		329	477	0.032	326	468	0.022	15
12		301	453	0.013	303	442	0.008	15
13		347	512	0.011	346	504	0.010	15

[a] Data collected in CHCl₃, unless otherwise specified. [b] In toluene.

As a result of the additional sterics inherent in functionalized polythiophenes, the emission is typically lower than that seen for the higher unfunctionalized oligothiophenes, with maximum Φ_F values of ~40%. For simple poly(3-alkylthiophene)s, the nature of the alkyl group has little effect on solution emission, as can be seen by comparing the values for polymers **6-9** of similar HT content. Branched side chains, however, can reduce packing in the solid state and result in modest increases in emission from thin films. Polymers of disubstituted thio-

phenes have also been investigated (**11-13**), although the increased sterics from the additional functional group results in significant blue shifts in absorbance and emission, as well as much lower Φ_F values.[15]

One unique property of polythiophenes is that it is possible to use sterics via a combination of choice of side chain and regioregularity to tune the colour of emission. Efforts by Inganäs and coworkers have shown that colour tuning spanning nearly the full visible spectrum is possible. It was only the deep green colours that the authors were unsuccessful in producing, as a result of the broad nature of the emission profile.[15]

4. Thiophene copolymers

A common method to increase the fluorescence of thiophene materials is the incorporation of thiophene as a component of copolymeric materials. As this reduces the total thiophene in the conjugated backbone, the effect of sulphur on ISC is potentially reduced, limiting loss to the triplet state and higher Φ_F values. As this subset of materials is extremely large, the scope of the discussion here is limited to the most common classes of such copolymers and materials in which thiophene makes up of at least 50% of the monomer content.

4.1 Thiophene-phenylene copolymers

The simplest examples of such copolymeric materials utilize benzene or functionalized benzene as a comonomer, as illustrated by the various copolymers **14-20** given in Fig. 6.[8,38-48] Not only does the addition of a non-sulphur-containing unit reduce the overall effect on ISC, but increases in the energy barrier for thienyl-phenyl rotations also contribute to reduced planarity[49a] and thus less efficient intermolecular packing. The combination of these effects can thus result in significant increases in fluorescence efficiencies as illustrated in Table 4.
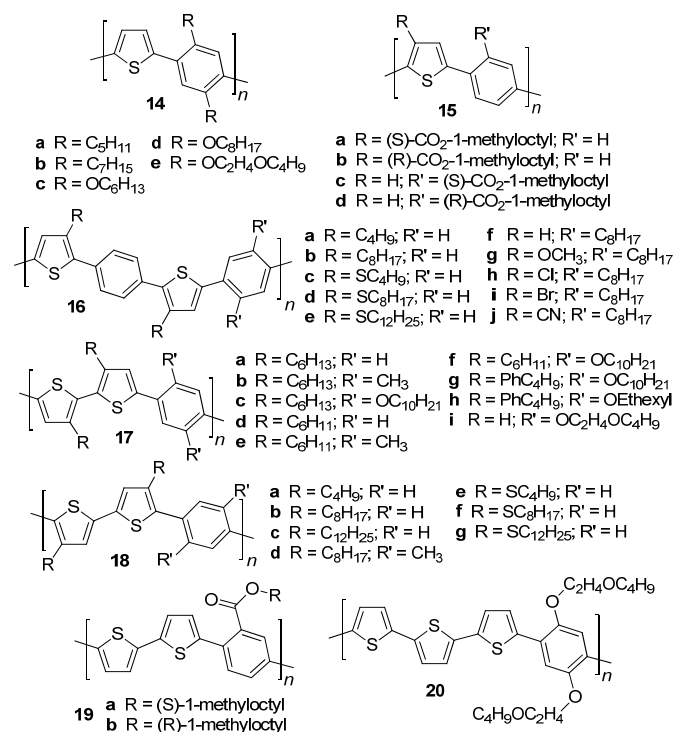

Fig. 6 Fluorescent thiophene-phenylene copolymers

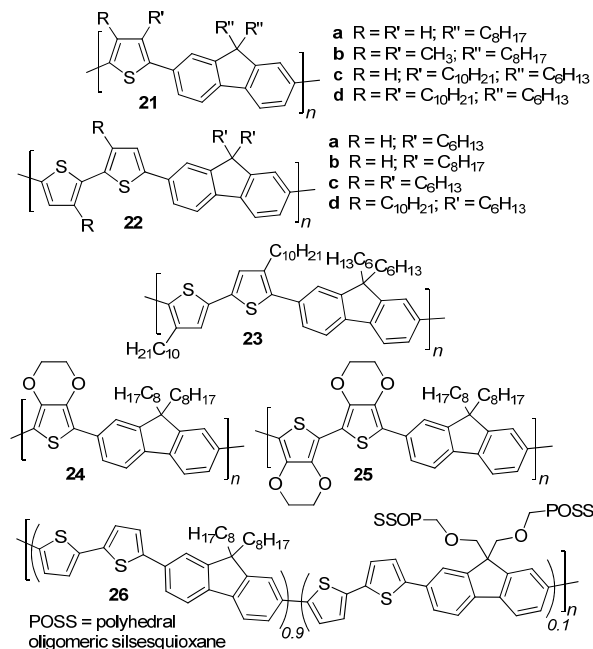**Table 4** Photophysical data for thiophene-phenylene copolymers

Polymer	Solution[a]			Thin film			Ref
	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	
14a	335	455					38
14b	330	460		322	459,496		39,40
14c		518		425	567		41
14d	460	525		427	538		42
14e	460	520	**0.87**	497	566,611		43
15a	369	480	0.18	383	493		44
15b	375	480	0.24	385	491		44
15c	390	494	0.24	412	520		44
15d	389	492	0.26	411	532		44
16a	388	488	0.48	388	517	0.17	45b
16b	386	488	**0.66**	388	512		45c
16c	400	510	0.25	410	530		45c
16d	396	510	0.33	390	526		45c
16e	396	510	0.23	390	526		45c
16f	406	476,506	**0.94**	437,470	467		45d
16g	446	536	0.25	470,509	540		45d
16h	384	478	**0.77**	400	492,510		45d
16i	382	488	0.40	401	484,507		45d
16j	384	480	0.60	388	532		45d
17a				396	524	0.20	46
17b				340	477	0.10	46
17c				430	530	0.29	46
17d				376	495	0.11	46
17e				360	466	0.06	46
17f				410	505	0.16	46
17g				442	532	0.11	47
17h	435	520		429	533	0.11	47
17i	476	543	0.47				43
18a	398	492	0.26	420	512		45a
18b	398	494	0.23	420	521		45a,c
18c	398	494	0.19	422	529		45a
18d	344[c]	469[c]	0.15	350	480		48
18e	408[b]	525[b]	0.44[b]	410	524		45c
18f	412[b]	523[b]	0.39[b]	420	524		45c
18g	416[b]	523[b]	**0.56**[b]	426	520		45c
19a	418	507	0.23	449	551		44
19b	420	509	0.23	443	557		44
20	478	547	0.42				43

[a] Data collected in CHCl$_3$, unless otherwise specified. Quantum yields over 50% are highlighted in bold. [b] In CS$_2$. [c] In THF.

The addition of the phenylene units, however, can also negatively affect the energies of absorbance. It has been proposed that the relative aromaticity of the conjugated units that make up the backbone determines the strength of the confinement potential of the π electrons within each of the aromatic rings. Because phenylene species are more aromatic than thiophene, the electron confinement within the ring becomes stronger and the delocalization length along the polymer backbone decreases.[4,10,13] As a result, most such phenylene copolymers exhibit blue-shifted absorbance in comparison to the polythiophene parents. This limitation, however, can be compensated by the inclusion of alkoxy groups on the phenylene units, which can result in polymers with absorbance and emission energies comparable or even red-shifted in relation to typical polythiophenes.

4.2 Thiophene-fluorene copolymers

Another common class of related materials utilize fluorene as the arylene unit, as illustrated by the polymers **21-26** given in Fig. 7.[49-52] As shown by the collected data in Table 5, this can result in highly fluorescent materials, with Φ_F values as high as 65%.[50] However, the increased phenylene content as a result of the biaryl structure of the fluorene unit results in reduced elec-

Fig. 7 Fluorescent thiophene-fluorene copolymers

tronic delocalization and a blue-shift in absorbance in comparison to the other materials discussed above.

Table 5 Photophysical data for thiophene-fluorene copolymers

Polymer	Solution[a]			Thin film			Ref
	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	
21a	431	496	0.49	438	490,515		49
21b				384	469		49
21c	403	461,(490)	0.41/**0.65**	412b	492,(477)		50
21d	367	447	0.25/0.39	378b	458,(475)		50
22a				450,(480)	560		51
22b	427	488	0.30	427	548	0.45	49,52
22c				396	493	0.32	50
22d	398	483,(520)	0.21/0.28	401	493,(520)		50
23	401	482,(515)	0.18/0.31	403	490,(520)		50
24				444	495,527		49
25				517	536,574		49
26				457	540	**0.66**	52

[a] Data collected in CHCl$_3$, unless otherwise specified. Values in parentheses are prominent lower energy shoulders. Quantum yields over 50% are highlighted in bold.

5. Fused-ring thiophene systems

Another popular approach to enhance the fluorescence of thiophene-based materials is the application of fused-ring units, especially fused 2,2'-bithiophenes such as cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT), dithieno[3,2-*b*:2',3'-*d*]silole (DTS), dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP), and dithieno[3,2-*b*:2',3'-*d*]-phosphole (DTPh) (Fig. 8).[4,7,53,54] The fused-ring nature of these species enhances the planar nature of the ground state,
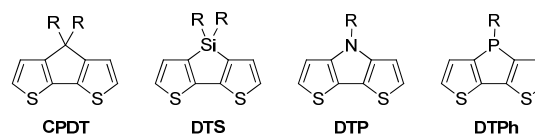
Fig. 8 Fused-ring bithiophene building blocks

while reducing the contributions of interannular torsional vibrations, both of which can lead to increased emission. An additional advantage of these units is that the central placement of the side chains allows the use of fairly bulky groups with little introduction of steric interactions that can result in reduced backbone planarity in the resulting materials.

5.1. Cyclopenta[1,2-*b*:3,4-*b'*]dithiophene (CPDT)-based materials

The oldest of these fused-ring species are cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT), with the monomeric species dating back to 1968.[55] Studies of the fluorescent properties of CPDT-based materials, however, did not really begin until the late 1990s with the characterization of various CPDT-based oligomers (Fig. 9).[56-58] The majority of these are fused-ring analogues of quaterthiophene (**Th$_4$**) and comparison of the data in Table 6 with that in Table 1 shows that the CPDT-based species exhibit red-shifts in both absorption and emission, with a modest increase in Φ_F.
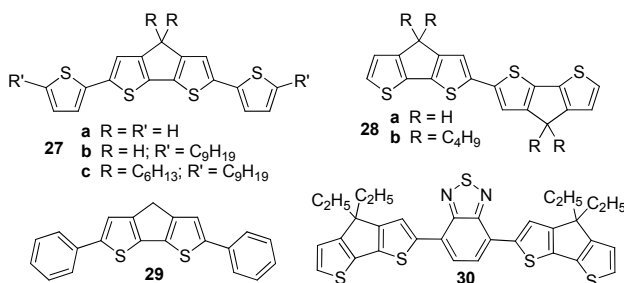

Fig. 9 Fluorescent CPDT-based oligomers

Both the red-shifts and increase in Φ_F are attributed to the increased rigidity of the CPDT unit, which results in a more planar backbone and reduced nonradiative deactivation of the excited state by interannular torsional vibrations.[56] Unfortunately, the CPDT unit was also found to be susceptible to photochemical decomposition, as evidenced by the presence of epoxide, hydroxyl, and carbonyl groups after the photolysis of oligomer **28b**.[56] Only **30** has been studied in the solid state, exhibiting only a 2 nm red-shift in the absorbance and complete quenching of the emission.[58]

Table 6 Solution photophysical data for CPDT-based oligomers[a]

Oligomer	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F[b]	Ref
27a	408	459,486	0.24	56,57
27b	415[b]	469[b]		59
27c	426[b]	481[b]		59
28a	416	467	0.14	56
28b	427	479	0.09	56
29	389	435	0.27	56
30	564	666	0.002	58

[a] Data collected in CHCl$_3$, unless otherwise specified. [b] In CH$_2$Cl$_2$.

In addition to the various oligomers, a number of CPDT-based polymers have also been reported (Fig. 10).[60-66] In terms of the homopolymeric materials (**31a-d**), both the absorbance and emission given in Table 7 are significantly red-shifted in comparison to typical polythiophenes, which is consistent with the increased planarization as a result of the fused-ring nature of the CPDT unit. At the same time, however, the fluorescence
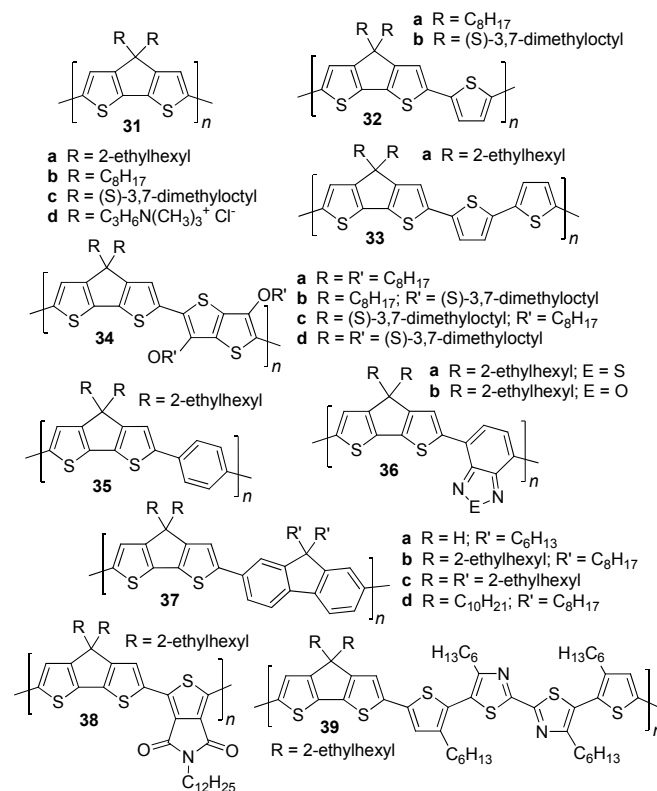

Fig. 10 Fluorescent CPDT-based polymers

quantum yields of these materials are very low, most likely due to a combination of the photochemical instability of the CPDT unit and enhanced interchain interactions as a result of increased planarity. Not surprisingly, the copolymers with arylene units gave the highest Φ_F values, with values as high as 40%.

Table 7 Photophysical data for CPDT-based polymers

Polymer	Solution[a]			Thin film		Ref
	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	
31a	574	650	0.01	613		60
31b	588[b]	653[b]	0.01	578		61
31c	588[b]	651[b]	0.01	581		61
31d	560	601,637				62
32a	588,625[b]	624b	0.04	573		61
32b	586,621[b]	624b	0.03	572		61
33	523	607	0.09	539		60
34a	612[b]	638[b]	0.07	596		61
34b	611[b]	641[b]	0.07	591		61
34c	571[b]	628[b]	0.13	593		61
34d	572[b]	636[b]	0.07	588		61
35	517	555	0.33	494		60
36a	693	773	0.01	722		60
36b	704	784	<0.01	701		60
37a	443	516	0.40	438	523	63
37b	489	539	0.22	483,518		60
37c	492	525	0.26	477,512		60
37d	404	561			545,590	64
38	652[b]	684[b]		670	727	65
39	466	569		466	583	66

[a] Data collected in THF, unless otherwise specified. [b] In CHCl$_3$.

5.2 Dithieno[3,2-*b*:2',3'-*d*]silole (DTS)-based materials

Another popular fused bithiophene in recent years has been the silicon analogue of CPDT, dithieno[3,2-*b*:2',3'-*d*]silole (DTS),
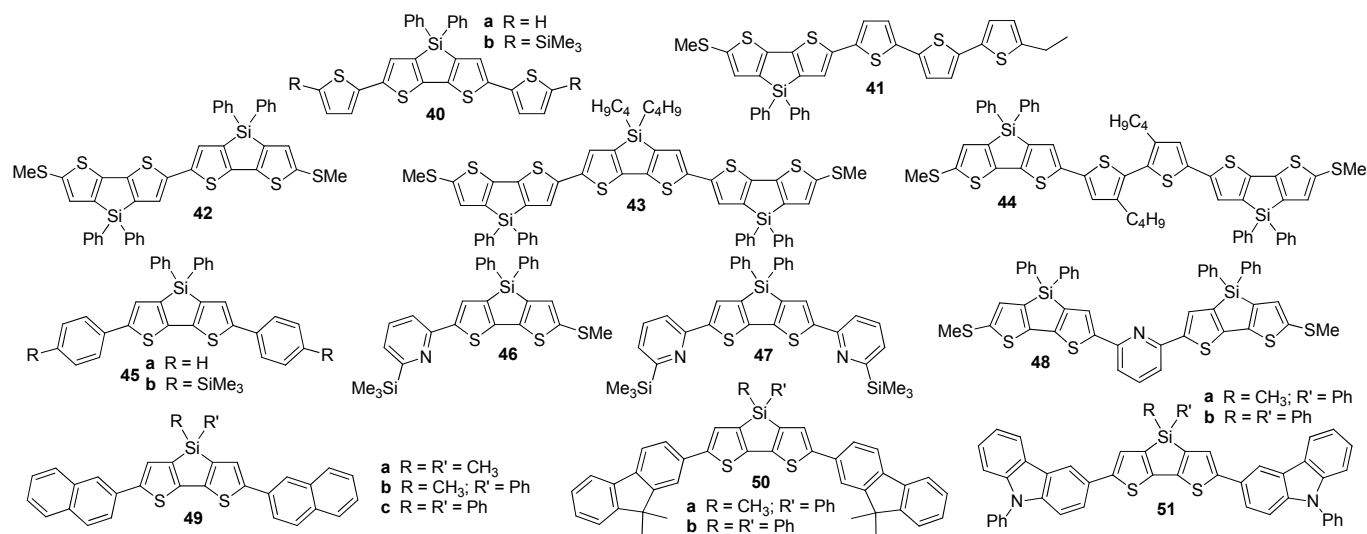
Ph Ph **a** R = H
b R = SiMe$_3$
R — 40 — R

MeS — 41 — Et (H$_9$C$_4$ C$_4$H$_9$)

MeS — 42 — SMe (Ph Ph Si; Ph Ph Si)

MeS — 43 — SMe (Ph Ph)

MeS — 44 — SMe (H$_9$C$_4$ ... C$_4$H$_9$)

R — 45 — R   **a** R = H   **b** R = SiMe$_3$

Me$_3$Si — 46 — SMe

Me$_3$Si — 47 — SiMe$_3$

MeS — 48 — SMe

49 — **a** R = R' = CH$_3$ **b** R = CH$_3$; R' = Ph **c** R = R' = Ph

50 — **a** R = CH$_3$; R' = Ph **b** R = R' = Ph

51 — **a** R = CH$_3$; R' = Ph **b** R = R' = Ph

Fig. 11 Fluorescent DTS-based oligomers

first reported by Ohshita and coworkers in 1999.[67] Various fluorescent DTS-based oligomers (**40-51**, Fig. 11) have since been reported, for which the collected photophysical data is given in Table 8.[68-71] It was expected that the silylene bridge would enhance the conjugation of the system via σ*-π* conjugation in the silole and enhance planarity as a result of the fused-ring nature of DTS.[68] Comparing the data in Table 8 with analogous oligothiophenes in Table 1 does show a red shift in solution absorption consistent with an increase in conjugation. In addition, the lack of significant red shifted absorption from solution to solid state for oligomers **49a-c** is consistent with enhanced planarity of the oligomer backbone.

As typical of thiophene materials, the synthetic versatility of the DTS-based species allows the production of materials with a wide range of emission colours, as illustrated in Fig. 12. Unfortunately, the DTS-based oligomers appear to exhibit lower emission yields than the parent oligothiophenes, with the lowest Φ_F values seen for those oligomers with the highest DTS content (i.e. **42**, **43**, and **44**).[69] As with the CPDT materials above,

it has been postulated that partial decomposition of the silole ring may play a role.[6] The addition of flanking fluorene or carbazole units, however, give emission yields as high as 80%.[71]

A number of DTS-based polymers have also been reported, as illustrated in Fig. 13.[72-75] As with the oligomers above, the polymers exhibit considerable red-shifts in both absorption and emission (Table 9) in comparison to typical polythiophenes (Table 3). In addition, comparing absorption spectra from solution to those in the solid state, only minor red shifts are observ-
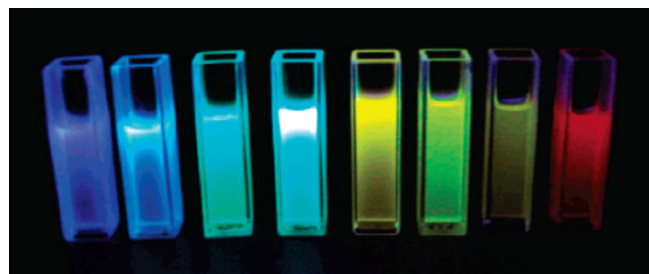
Fig. 12 Range of emission colours from solutions of various DTS derivatives [Reprinted with permission from D.-H. Kim, J. Ohshita, K.-H. Lee, Y. Kunugi, and A. Kunai, *Organometallics* 2006, **25**, 1511. Copyright 2006 American Chemical Society]

Table 8 Photophysical data for DTS-based oligomers

Oligomer	Solution[a]			Thin film		Ref
	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	
40a	426	518				68
40b	435	505,532				68
41	451	520	0.15			69
42	453	533	0.15			69
43	498	576	0.08			69
44	436	544	0.02			69
45a	409	495				68
45b	417	479,500				68
46	400	500	0.20			69
47	418	480,498				68
48	395	498	0.22			69
49a	421	481	0.32	425	521	70
49b	423	484	0.27	427	528	70
49c	426	491	0.21	431	532	70
50a	434[b]	498[b]	0.31[b]			71
50b	436[b]	503[b]	0.35[b]			71
51a	429[b]	501[b]	**0.80[b]**			71
51b	427[b]	508[b]	0.46[b]			71

[a] Data collected in THF, unless otherwise specified. Quantum yields over 50% are highlighted in bold. [b] In CH$_2$Cl$_2$.

Table 9 Photophysical data for DTS-based polymers

Polymer	Solution[a]			Thin film			Ref
	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	
52a	545	633		546			73
52b	561	641		580			73
53a	555[b]	628		546			73
53b	546[b]	630		565			73
53c	483	612		493			73
54a	529	612		554			73
54b	532	611		558			73
54c	482	592		490			73
55a	410,675[b]	729[b]					74
55b	429,717[b]	798[b]					74
56	416[b]	513[b]	0.16[b]	420	560	0.06	75
57	418[b]	491[b]	0.36[b]	433	609	0.08	75

[a] Data collected in THF, unless otherwise specified. [b] In CHCl$_3$.
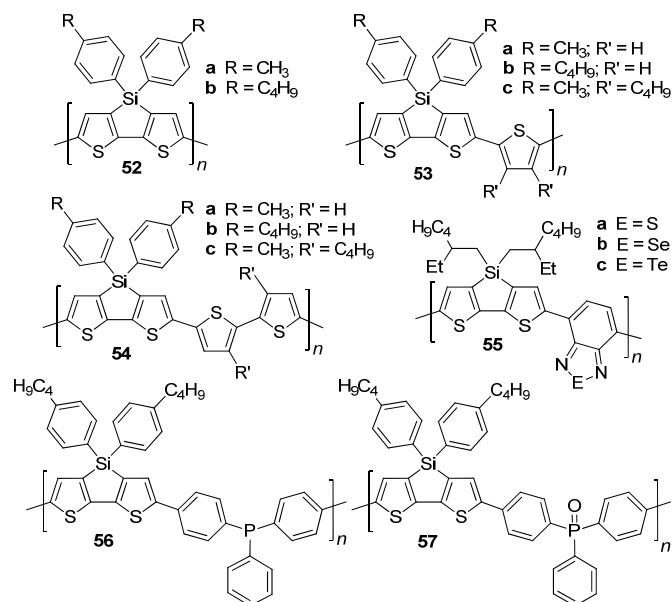
Fig. 13 Fluorescent DTS-based polymers

Fig. 14 Fluorescent DTP-based oligomers

ed. Both trends are again consistent with increased conjugation and planarity as a result of the DTS unit. Unfortunately, the emission quantum yields have not been determined for the majority of these materials, although a moderate Φ_F value of 36% was determined for polymer **57**.[75] Random copolymers of DTS and fluorene have also been reported, but the DTS content in both samples studied is quite low (5% or lower).[72]

5.3. Dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP)-based materials

Perhaps one of the most successful approaches to improve the fluorescence of thiophene materials has been the application of dithieno[3,2-*b*:2',3'-*d*]pyrroles (DTP), first reported by Zanirato and coworkers in 1983.[54,76] These materials did not really become widely studied, however, until their reintroduction by Rasmussen and coworkers in 2003,[54,77] and a large number of DTP-based oligomers and polymers have since been reported.[54] In terms of their emission properties, a number of highly fluorescent DTP-based oligomers have been reported (Fig. 14).[59,78-83] As shown in Table 10, these exhibit similar absorption red shifts as a result of the planar nature, although to a lesser extent than that exhibited by the DTS analogues above.

Although monomeric DTPs are very weak emitters,[54] many of the oligomers included in Table 10 exhibit relatively strong solution fluorescence, with the majority of these providing Φ_F values of 50% or greater. The strength of the reported emission has made these DTP-based oligomers some of the strongest emitting examples of thiophene-based materials. This increased emission has been attributed to both decreased nonradiative deactivation via interannular torsional vibrations as a result of the fused-ring unit and the general photochemical stability of the DTP unit.[79] While it would be expected that these effects would be maximized in the DTP dimer **61**, its emission efficiency is low in comparison to the DTP-based quaterthiophenes **59a–f**. This could perhaps be attributed to the increased alkyl side chain density, thus resulting in a greater number of high frequency modes and therefore more deactivation pathways via internal conversion.[79] Similar effects can be seen in the photophysical properties of oligomer **59e** and this also explains the high Φ_F values exhibited by the N-phenyl derivatives.
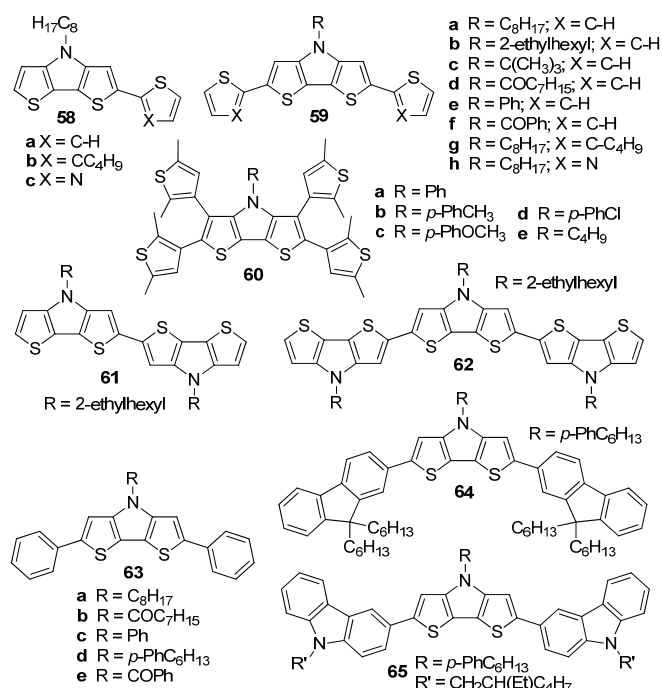
The most recent DTP units have incorporated N-acyl groups (**59d**,**59f**,**63b**,**63e**) which result in stabilized HOMO levels and large increases in fluorescence efficiency.[80,84] It has previously been shown that the addition of carbonyl groups to oligothiophenes results in reduced nonradiative decay and increased Φ_F, which was proposed to be due to an increase in conjugation and thus a decrease in intersystem crossing. The application of the

Table 10 Photophysical data for DTP-based oligomers

Oligomer	Solution[a]			Thin film			Ref
	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F^b	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	
58a	364,(383)	421	0.29				79
58b	341	420	0.089				79
58c	378,(390)	418	**0.55**				79
59a	404	444,470	0.49	404,(434)	502	0.0024	79
59b	405	443,470	**0.60**	405,(434)	501	0.0020	79
59c	403	444,470	**0.66**	409,(436)	499	0.021	79
59d	399[c]	446,468[c]	**0.68**[c]	417,(444)			80
59e	396[c]	444[c]	**0.70**[c]				80
59f	398[c]	440[c]	**0.73**[c]	409,(430)			80
59g	382	446,472	0.36				79
59h	413,433	451,478	**0.54**				79
60a	348	417	0.14				78
60b	349	410	0.16				78
60c	349	418	0.13				78
60d	349	422	0.14				78
60e	350	417	0.18				78
61	410	462,488	0.37	414			82
62	464	525,560	**0.72**	468			82
63a	381[c]	446,468[c]	**0.53**[c]	393,(420)			80
63b	380[c]	424,439[c]	**0.62**[c]	406,430			80
63c	396[c]	421,440[c]	**0.87**[c]	354,(414)			80
63d	379[d]	423,444[d]	**0.57**[d]	400	468,520		81
63e	380[c]	424[c]	**0.92**[c]	381,(419)			80
64	416[d]	464,491[d]	**0.75**[d]	422	481,505	0.22	81,83
65	401[d]	446,473[d]	**0.52**[d]	413	485		81

[a] Data collected in CHCl₃, unless otherwise specified. Values in parentheses are prominent lower energy shoulders. Quantum yields over 50% are highlighted in bold. [b] In cyclohexane. [c] In CH₃CN. [d] In THF.

acyl group to DTP-based oligomers has been shown to be able to double the Φ_F, with maximum values of 92%. The greatest gains in efficiency resulting from the N-acyl group seem to be seen in oligomers exhibiting weaker fluorescence with other functionalities.

The fluorescence properties of a number of DTP-based polymers have also been reported (Fig. 15) and the corresponding photophysical data is given in Table 11.[85-91] It should be noted that the materials in Fig. 15 represent a relatively small fraction of the DTP-based polymers reported in the literature and that the majority of these materials have not been characterized in terms of any potential emissive properties.[54] As with the analogous oligomers above, the DTP-based polymers exhibit higher Φ_F values than typical polythiophenes, with values as high as 56%. In addition, many of these materials emit various shades of red, a colour that is difficult to achieve with more common strongly conjugated emitters.

Emissive properties of a few of the DTP-based polymers discussed here have also been characterized in the solid state. For the homopolymers, solid state emission is almost completely quenched as a result of the increased planarity and strong interchain interactions of the DTP unit, both of which should favour close-packed structures.[92] Such close-packed structures can be inhibited by copolymerization with arylene units (i.e. **67-70**), thus resulting in reported solid-state Φ_F values as high as 26%. As can been seen in Table 11, even with this structural limitation, a fair amount of colour tuning is still possible.

5.4. Dithieno[3,2-*b*:2',3'-*d*]phosphole (DTPh)-based materials

Another quite successful approach to thiophene materials with improved fluorescence has been the application of the phosphorous analogue of DTP, dithieno[3,2-*b*:2',3'-*d*]phosphole (DTPh), first reported by Baumgartner and coworkers in 2003.[53,93] In contrast to DTP, which contains a planar sp[2] hybridized nitrogen, the phosphorous center of DTPh is pyramidal.[53] As a result, the phosphorous lone pair only weakly interacts
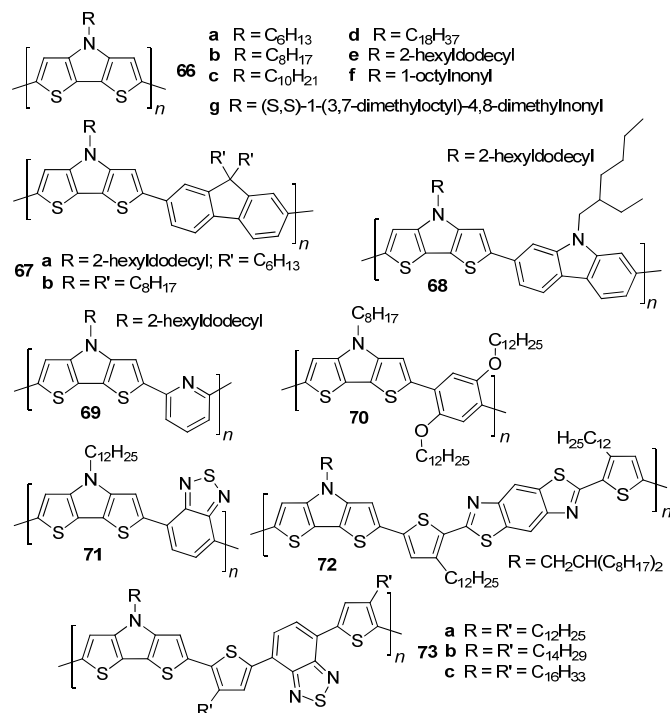
Table 11 Photophysical data for DTP-based polymers

Polymer	Solution[a] λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	Thin film λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	Ref
66a[b]	543	612	0.27	551			85
66b[b]	550	612	0.31	555			85
66b[c]	522	602	0.18	526			86
66c[b]	552	614	0.31	572	[f]		85
66d[b]	553	617	0.27	561			85
66e[d]	533	610	0.39	553	655	0.03	87
66f[c]	544	617	0.25	541			86
66g[c]	551	617	0.28	555			86
66g[d]	549	618	0.32	547			86
67a	486	518	**0.56**	481,510	536,566	0.26	87
67b	487[e]	531	**0.50**	484,512	536,567		88
68	466	513	**0.51**	477	590	0.19	87
69	421	511	0.34	440	549	0.23	87
70	526[e]	565	0.37	529,566	601		88
71	596[e]	695		620			89
72	563	600		560	[f]		90
73a	624[e]	758		698			91
73b	613[e]	763		685			91
73c	608[e]	773		673			91

[a] Data collected in THF, unless otherwise specified. Quantum yields over 50% are highlighted in bold. [b] Polymerized via FeCl$_3$. [c] Polymerized via RuCl$_3$. [d] Polymerized via Stille or Suzuki coupling. [e] In CHCl$_3$. [f] Thin film fluorescence not observed or too weak to measure.

with the conjugated π-system resulting in a low degree of delocalization of the phosphorous electrons.[53,93] Because of this chemical difference, the DTPh phosphorous can still act as a sufficient Lewis base and is able to react with oxidizing agents or Lewis acids to offer a variety of methods for the tuning of the resulting optical and electronic properties.[94]

As shown in Table 12 and Fig. 16, a number of highly fluorescent DTPh-based oligomers have been reported.[53,94-101] As with the previously discussed DTP-based oligomers, the

Fig. 15 Fluorescent DTP-based polymers

Table 12 Photophysical data for DTPh-based oligomers

Oligomer	Solution[a] λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	Thin film λ_{max}^{em} (nm)	Φ_F	Ref
74	432	525	**0.58**			95
75a	460	520	0.36			94
75b	445	519	**0.68**			94
75c	452	529	**0.63**			94
75d	473	601	**0.56**			95
75e	527	566	0.48			94
75f	515	657	0.39			96
76	485	545	0.43			94
77	456,488	456	0.37			94
78	438,(520)	560,(605)	0.31			97
79	486	535	0.38			94
80	471	516	0.20			98
81	457	562	0.15			98
82	474	631	0.25			99
83	489	628	0.24			99
84	465	544	**0.80**			100
85	428	498	0.32			100
86	416	489	0.21			100
87	430	500	0.19			100
88	421	512	0.21			98
89a	438	535	**0.77**	533	0.30	101
89b	463	577	**0.79**	579	0.14	101
89c	417	519	**0.57**	535	0.40	101

[a] Data collected in CH$_2$Cl$_2$, unless otherwise specified. Values in parentheses are prominent lower energy shoulders. Quantum yields over 50% are highlighted in bold.

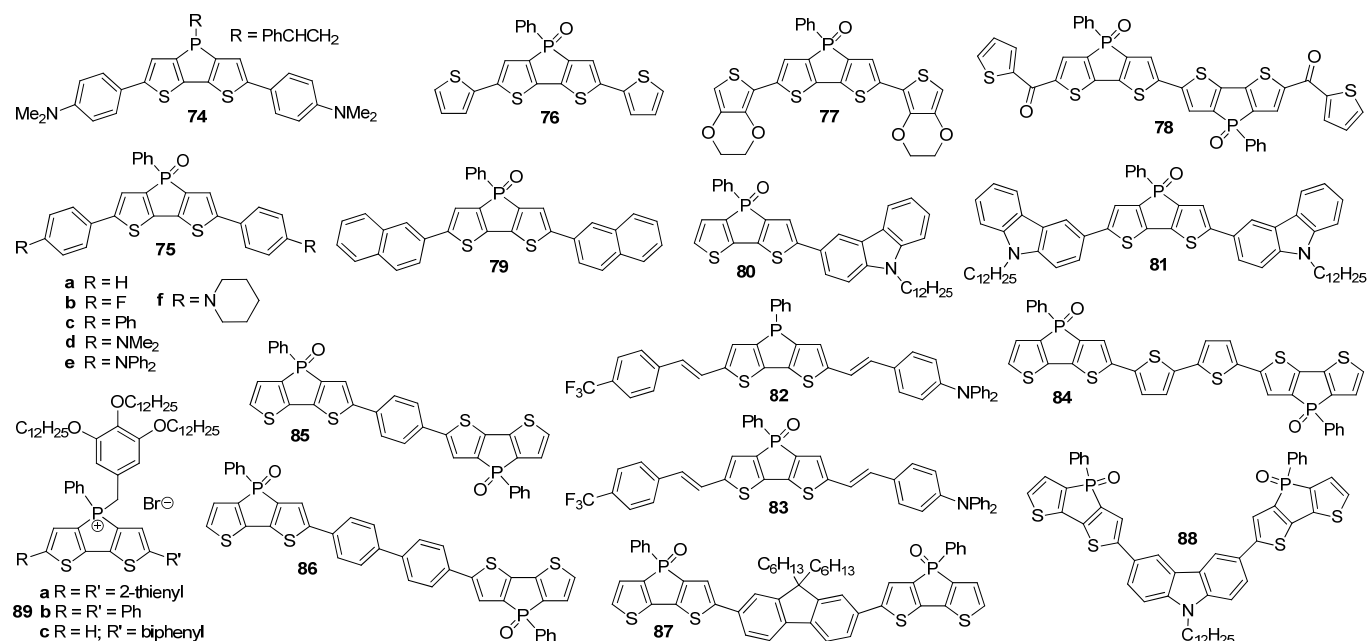**Fig. 16** Fluorescent DTPh-based oligomers

majority of these DTPh-based materials provide Φ_F values of 50% or greater. As with the other fused-ring systems, the enhanced fluorescence is largely attributed to the rigid structure of the fused-ring system, thus reducing loss via IC.[102] As can be seen in Fig. 16, many of the DTPh oligomers utilize the phosphorous oxide forms of DTPh. Here, oxidation of the phosphorus to generate the corresponding oxide results in a red-shift in both the absorption and emission of the corresponding oligomer, with little to no effect on Φ_F. In addition, the sp³ hybridization of the phosphorous center also allows the inclusion of a second bulky group on the phosphine, thus allowing the production of phospholium salts capable of forming highly fluorescent organogels, as illustrated by oligomers **89a-c**.[101]

Although the homopolymeric DTPh materials have not yet been reported, DTPh has successfully been incorporated into various copolymers as illustrated in Table 13 and Fig.

17.[93,94,98,102,103] As with many of the oligomers shown in Fig. 16, all of the polymers utilize either the phosphorous oxide or quaternary phosphorous derivatives of DTPh. While quantum yields have only been determined for a few polymers, the available data again indicates stronger fluorescence than analogous materials of traditional thiophenes.

Table 13 Photophysical data for DTPh-based polymers

Polymer	Solution[a]			Thin film		Ref
	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_F	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	
90	515	546	0.48			94
91	463	624	0.02			98
92	456,502	555				93
93	345,485	509,540	0.47	527	556	102
94a	468	607		533	676	103
94b	472	610		531	677	103
94c	480	613		535	685	103
94d	481	612		529	693	103

[a] Data collected in CH_2Cl_2, unless otherwise specified. [b] In $CHCl_3$, data for the high molecular weight fractions.

6. Applications

6.1. Organic Light-Emitting Diodes (OLEDs)

Although other electroluminescent materials outperform them in many ways, thiophene-based materials allow good control of OLED colour[8] and can easily produce red colours, which are difficult to achieve with materials such as poly(phenylene vinylene)s, poly(p-phenylene)s, or polyfluorenes.[6,7] Thiophene-based materials were first applied to OLEDs in 1991, with the report by Yoshino and coworkers of red-orange emitting devices utilizing polymer **7** and analogous poly(3-alkylthiophene)s utilizing even longer sidechains.[6,7,104] The schematic structure of a typical OLED device is illustrated in Figure 18a. Following this, a number of polythiophene-based devices were reported, all emitting in the range of 590-670 nm, but with relatively low electroluminescence quantum yields (although a
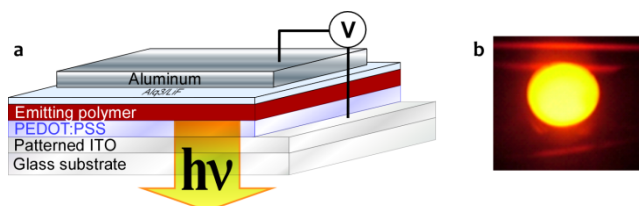

Fig. 17 Fluorescent DTPh-based polymers

Fig. 18 Schematic structure of a typical OLED device (**a**) and electroluminescence from an OLED of polymer **67b** (**b**).

few examples have given values above 0.1%).[6,7] Not surprisingly, thiophene copolymers have allowed greater colour tunability and higher efficiencies, with significant focus on both thiophene-phenylene and thiophene-fluorene copolymers. Here, the reduced thiophene content, along with less efficient solid state packing, allow greater thin film Φ_F values and higher OLED efficiencies. One of the most successful examples from such materials includes the thiophene-phenylene copolymer **14b**. Devices of **14b** emit blue light of 477 nm with an efficiency of 0.2%. However, it was found that blending **14b** with poly(2,5-diheptyl-2',5'-dipentoxybiphenylene) resulted in significant increases in device efficiency. Thus blends utilizing 10% **14b** resulted in a slightly blue-shifted emission at 460 nm with an efficiency rise to 2%.[105]

Considering the high solution and solid-state emission efficiencies reported for the fused-ring thiophene systems discussed above, it is somewhat surprising that the application of these materials to OLED devices has been somewhat limited. The earliest report of applications of these materials as emitting layers in OLEDs was in 2007 and utilized the homopolymer **52b** and the copolymers **53c** and **54c**.[73] While these devices successfully afforded red emission, the luminance was quite low (<6 cd/m^2). The device of copolymer **53c** was found to be improved with the addition of an electron-transporting tris(8-quinolinolato)aluminium(III) (Alq$_3$) layer, increasing the luminance to 75 cd/m^2 (Table 14). The threshold voltage, however, was still quite high and it has been proposed that the low performance may be due to partial decomposition of the silole.[6]

Table 14 Data for OLED devices utilizing fused-ring thiophene materials

Material	λ_{max}^{EL} (nm)	$E_{threshold}$ (V)	Max luminance (cd/m^2)	Ref
37c	542,578	2.0	20,000	64
53c	649	11	75	73
66c	647	6.0	12	88
67b	541,577	5.2	197	88
70	647	5.9	30	88
73a	795	3.0		91
73b	780	3.7		91
73c	814	4.0	54	91

Devices utilizing random copolymers of DTS and fluorene have also been reported, which give quite successful results.[6,72] These OLEDs emitted green light with a luminance of 13,100 cd/m^2 and an efficiency of 0.41%.[72] In this case, however, the DTS content is quite low (5% or lower) and thus these are more characteristic of a polyfluorene device. It should be noted that while DTS-based materials have not found much success in light-emitting materials in OLEDs, they have found to be good electron-transport materials for such devices.[67,68,70]

The use of DTP-based emitters in OLEDs was first reported by Patri and coworker in 2009.[91] This study utilized copolymers **73a–c** to generate red emitting OLED devices (Table 14). This was then followed by a second report in 2010 by

Rasmussen and coworkers, which utilized the homopolymer **66c** and the copolymers **67b** and **70** to give devices with emissive colours that ranged from yellow-green (Fig. 18b) to red-purple.[88] Here, the DTP homopolymer gave the poorest performing devices with both the highest threshold voltage and lowest maximum luminance (Table 14), primarily due to the increased planarity and the strong interchain interactions of the DTP-based species resulting in close-packed structures and thus emission quenching in the thin films.[88] However, in both studies the application of copolymers containing arylene units limits the extent of close-packing and thus allows the fabrication of more successful devices. Of such copolymers, the initially studied **73a–c** gave the lowest reported threshold voltages, but only moderate luminance was reported for **71c**.[91] In comparison, the DTP-fluorene material **67b** gave higher threshold voltages, but nearly four times the maximum luminance with a maximum efficiency of 0.8 Lm/W.[88] A possible limitation in device performance for the DTP-based materials may be the high HOMO energy levels of these materials, which is currently being addressed via the recently reported N-acyl derivatives which significantly stabilize the HOMO levels.[80,84]

Quite recently, OLEDs utilizing the CPDT-based copolymer **37c** as the emitting layer were reported that exhibit by far the best performance of any of the fused-ring systems.[64] While the reported colour was orange, the electroluminescence spectral profile is nearly identical to the DTP analogue **67b**. The devices, however, exhibited threshold voltages of only 2.0 V, luminance up to 20,000 cd/m^2, and a maximum current efficiency of 2 cd/A. Overall, while the success of red-light-emitting phosphorescent dye-doped OLEDs may limit the importance of thiophene-based materials as red emitters, the synthetic versatility of these materials still make them very attractive building blocks for creating light-emitting materials with tailored properties.[6,7]

6.2. Fluorescent dyes for biological labelling

Oligothiophenes have also recently found successful application as fluorescent dyes for the labelling of various biological molecules, as pioneered by the group of Barbarella.[106-112] As such fluorescent markers, oligothiophenes have a number of attractive characteristics, most notably their tunable fluorescence as discussed above.[106] Additional merits include large extinction coefficients, large energetic differences between absorption and emission wavelengths, and relatively good fluorescence efficiencies.[106] Oligothiophenes are also considered to be generally non-toxic, which makes them particularly suitable for cellular staining and fluorescence microscopy applications (Fig. 19).[107] Lastly, for some derivatives, the fluorescence has been shown to be sensitive to the microenvironment, which can then be used to probe variations in this environment and thus corresponding biochemical processes.[107]

For the majority of these labelling applications, the oligothiophenes are derivatized with reactive groups which can then undergo bond-forming reactions with free units (-NH$_2$, -OH, etc.) of the biological species to be labelled. To date this has included isothiocyanates,[108] N-succinimidyl esters,[109] 4-sulfotetrafluorophenyl esters,[110] phosphoramidites, and azides.[ii] Further methods for the application of oligothiophenes as fluorescent biomarkers have also included the production of oligothiophene derivatives of deoxyuridine, which could then be incorporated into an oligonucleotide sequence for application as probes for the detection of specific mutations,[111] and oligothiophene-labelled nanoparticles for the staining of cells.[112]
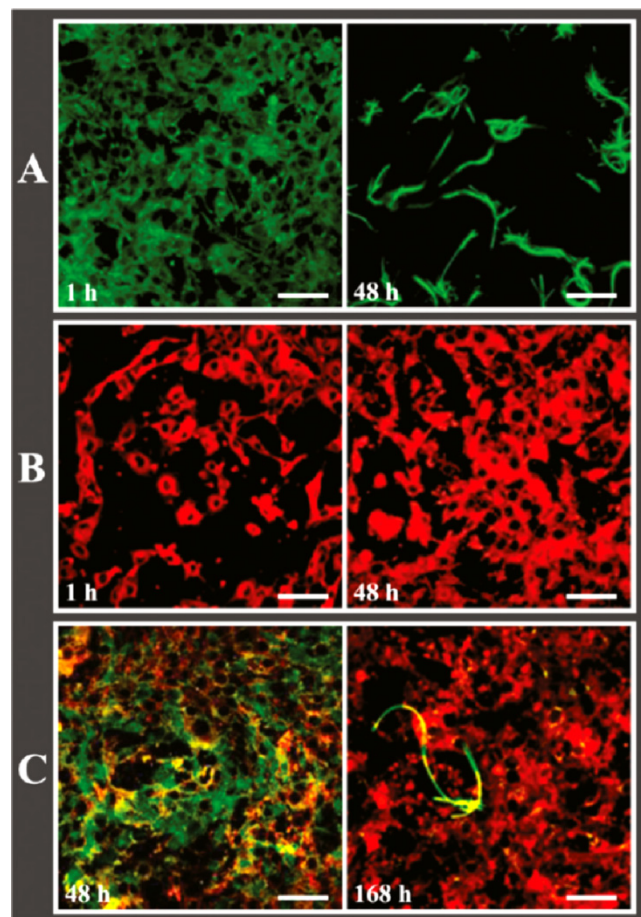
Fig. 19 Laser scanning confocal microscopy images of NIH 3T3 cells stained with various oligothiophenes at specified time periods after treatment and extensive washing [Reprinted with permission from I. Palam, F. Di Maria, I. Viola, E. Fabiano, G. Gigli, C. Bettini, and G. Barbarella, *J. Am. Chem. Soc.* 2011, **133**, 17777. Copyright 2011 American Chemical Society].

6.3. Fluorescent Sensors

Fluorescent thiophene-based materials have also been investigated for various applications as sensing materials in which an analyte is detected due to either emission quenching or a shift in the emission energy.[113] Such applications are typically in solution, the most simple of which involves the selective detection of metal ions via emission quenching. Examples of such sensing include applications of a thiophene-phenylene copolymer to selectively detect mercury in concentrations as low as 20 ppb.[114] In a similar fashion, a thymine-functionalized polythiophene was also able to selectively detect mercury,[115] and selective detection of copper was found by a diester-functionalized polythiophene,[116] while a quinoline-functionalized polythiophene was less selective and exhibited emission quenching by Cu^{2+}, Cd^{2+}, and Pb^{2+}.[117] Finally, one group used the emission quenching of a cationic, water-soluble polythiophene by Cu^{2+} to produce a "turn on" sensor for catechins (flavonoids found in green tea).[118] In this case, the polymer is initially treated with Cu^{2+} to quench the emission. In the presence of catechins, however, the emission is recovered due to the flavoniods selectively removing the ions from the polymer. In all of these cases, it is believed that the fluorescence quenching is due to ion-induced aggregation of the polymer chains.

A similar approach has also been utilized for the detection of various small molecules. In most cases, these are polythio-

phenes containing charged side chains which result in water-soluble materials. In the presence of appropriate analytes, co-operative effects result in either a conformational change in the backbone or aggregation effects, thus changing the polymer emission or quenching it altogether. This approach has been used for the production of selective sensing of lysophosphatidic acid,[119] cysteine,[120] carbenicillin,[121] and anionic surfactants.[122] Various thiophene-based materials have also been investigated for the detection of TNT and its derivatives.[66,123]

Finally, various cationic polythiophenes have been used in the detection of DNA and various proteins.[113,124-128] These efforts have been largely carried out by the group of Mario Leclerc[125] and unlike the previous detection methods described above, utilize "turn on" processes or fluorescence enhancement as the sensing mode. These efforts have clearly demonstrated the potential of fluorescent biosensors based on hybrid DNA-polythiophene electrostatic complexes, particularly for the PCR-free detection of DNA.[125a]

Conclusions

As can be seen from the wealth of materials presented above, thiophene-based materials allow a high degree of structural versatility and thus a wide range of tunability. While the parent oligo- and poly-thiophenes exhibit limited fluorescence efficiencies, a range of approaches have been developed over the last decade that allow the generation of highly fluorescent thiophene-based materials. The primary factors leading to low fluorescence are efficient intersystem crossing as a result of the thiophene sulphur (usually attributed to the heavy atom effect), relaxation of the excited state via interannular rotations within the backbone, and quenching as a result of aggregation effects. As such, the most successful approaches to enhancing fluorescence has been the introduction of structural changes that limit these effects — primarily replacement of some of the thiophene content with other conjugated units in order to reduce the overall sulphur content, introduction of sterics to reduce aggregation and efficient packing, and the incorporation of fused ring units to reduce possible interannular rotation.

The most successful of these approaches has been the utilization of the fused-ring bithiophene units, particularly when incorporated into copolymeric frameworks, thus addressing all three of the primary limiting factors given above. Unfortunately, both the carbon and silicon bridged units seem to suffer from photochemical instability. However, this is not a limitation for the nitrogen and phosphorous analogues and the application of these species has successfully resulted in fluorescent materials with solution quantum efficiencies as high as 92% and thin film values as high as 26%.

While these newer materials based on the successful fused-ring systems have yet to be significantly utilized in emissive applications, the more traditional materials have shown great promise in both biological labelling and sensing applications. Such promise, coupled with more recent advances in producing more highly fluorescent materials and the overall tunability inherent in thiophene-based systems, provides ample motivation to continue the study and utilization of these materials for emissive applications.

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Notes and references

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