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Azadipyrromethenes: from traditional dye chemistry to leading edge applications.

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Azadipyrromethenes: From Traditional Dye Chemistry to Leading Edge Applications

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Azadipyrromethenes were first described over 70 years ago as blue pigments, but now are rapidly emerging as a compound class with highly desirable near infrared photophysical properties. Since the turn of the century several routes to azadipyrromethenes have been developed and numerous post-synthesis derivatizations have allowed for their exploitation in both biological and material sciences. The relative ease of access to specifically designed derivatives is now allowing their use in multiple technological formats from real-time fluorescence imaging, to solar energy materials, to optoelectronic devices and many more. In this review we have highlighted the synthetic component of this story as it is the ability to generate the designer azadipyrromethene that opens the door to exciting applications.

1 Introduction

Research interest in utilizing the (Z)-N-(2H-pyrrol-2-ylidene)-1H-pyrrol-2-amines, better known as azadipyrromethenes, has rapidly grown since the turn of the century. Whilst the first reports of their synthesis and properties can be traced to the first half of the last century, the more recent strong re-emergence in interest can be attributed to their accessibility from several synthetic routes and their ability to be modified post-synthesis (Fig. 1).[1,2] This has permitted the development of structurally tailored derivatives, delivering a wide range of application specific properties to the compounds to suit the researchers' goals. Such applications included in this review are near-infrared fluorochromes, fluorescent sensors, energy/electron transfer cassettes, nanoparticle conjugates, donor/acceptor conjugates for solar cell applications, optoelectronics, light activated therapeutics, and supramolecular building blocks. In this review we have confined ourselves to the structural scaffold as shown in Fig. 1 as the related dipyrromethenes have been previously expertly reviewed.[3]

The primary focus of this review is on the different synthetic approaches to the azadipyrromethene scaffold and their post-synthesis modification.

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Donal O'Shea received his Ph.D. degree in Chemistry from University College Galway in 1994. He held post-doctoral positions in the University of Edinburgh and Carnegie Mellon University, Pittsburgh following which he was a research scientist at Eastman Kodak Company in Rochester, New York. In 1999 he returned to academia to a position in University College Dublin and was promoted to associate Professor of Chemistry in 2007. He moved to the Royal College of Surgeons in Ireland as Prof of Chemistry in 2013. His research interests include organometallic chemistry, light activated therapeutics and near-infrared fluorophores as research tools and for fluorescence guided surgery.

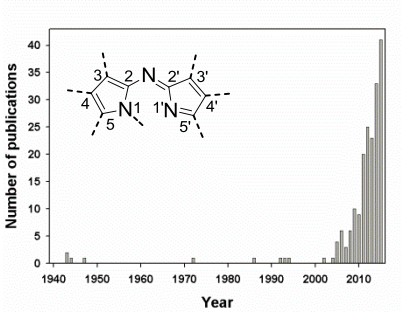
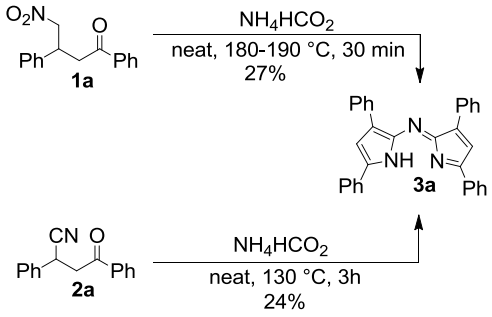


Fig. 1 Structural scaffold of azadipyrromethenes and yearly number of publications dealing with azadipyrromethenes according to SciFinder Scholar structure search (reviews not included) performed in January, 2016.

These synthetic tools allow the production of azadipyrromethenes with designed and tailored properties which are tabulated by specific application at the end of the review. Table data includes photophysical properties, NIR-optical sensors , bio- and material-conjugates, photodynamic therapy agents, photoredox catalysts, solar energy materials, and optoelectronic materials.

2 Synthetic strategies for azadipyrromethenes

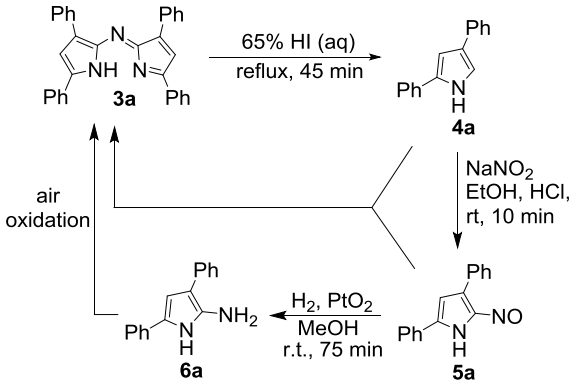
The synthesis of azadipyrromethene **3a** was first reported in 1943 by M. Rogers while working for Imperial Chemical Company (ICI) Dyestuffs LTD in Blackley, Manchester, U.K. (Scheme 1).[1,2,4] His discovery was the unexpected result of an attempted Leuckart reaction conducted by heating ammonium formate with 4-nitro-1,3-diphenylbutan-1-one **1a** under solventless conditions.[1] Rather than the anticipated reductive amination product, an intense blue colour was observed from the reaction with a similar coloured result obtained when 4-oxo-2,4-diphenylbutanenitrile **2a** was used as substrate (Scheme 1).[4]



Scheme 1 Synthetic routes to azadipyrromethene developed by Rogers.

Rogers' motivation to deduce the source of the observed colour is understandable considering the importance of the dye industry at that time to his employer. It is of interest to note that in his abstract he describes **3a** as "a new chromophoric system, having a formal relationship to the phthalocyanines" which had been industrially developed by ICI Grangemouth division in 1929 and remains today as one of the most important industrial blue pigments. It could be speculated that the huge success of the phthalocyanine dyes may have contributed to the lack of interest in azadipyrromethenes for the following 50 years.

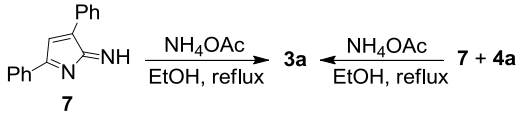
Considering the increase in structural complexity of product **3a** from either starting substrate **1a** or **2a**, the structural assignment of the coloured product would not have been trivial at that time. With analytical instrumentation of that era largely limited to melting points, elemental analysis, and molecular weight determinations, structural assignments were often elucidated by characterization of products from degradation reactions and by development of alternative synthetic routes. The matrix of product degradation and re-synthesis adopted by Rogers is shown in Scheme 2.[1,4]



Scheme 2 Degradation and re-synthesis of tetraphenylazadipyrromethene.

The key degradation reaction involved heating of **3a** with hydriodic acid which produced 2,4-diphenylpyrrole **4a**, a precursor compound of which had been previously reported in the literature in 1925.[5] This result permitted two additional routes to be devised, both of which provided the unknown compound **3a**. Conversion of **4a** into 5-nitroso-2,4-diphenylpyrrole **5a** was achieved with sodium nitrite which in turn could be condensed with **4a** to generate **3a,** thereby confirming its structure. Additionally, reduction of nitroso pyrrole **5a** with Adams's catalyst produced the corresponding 5-amino-2,4-diphenylpyrrole **6a** which upon exposure to air oxidised and self-condensed with the loss of ammonia resulting in the formation of **3a**, albeit in very low yield. In this first report nine different tetraarylazadipyrromethenes were described using these routes.[1]

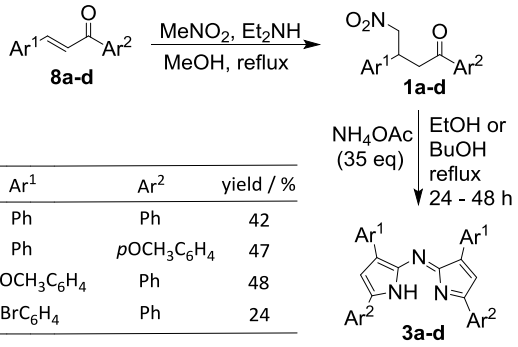
Work for our laboratory utilising ^{15}N labelling with $^{15}NH_4OAc$ as ammomia source and the rational synthesis of specifically ^{15}N labelled derivatives of **4a** and **6a** showed that in the overall conversion of **1a** into **3a**, two related pathways are ongoing concurrently; the first involves a dimerization of *in situ* formed 3,5-diphenyl-2*H*-pyrrol-2-imine **7**, and the other reaction of **7** with 2,4-diphenylpyrrole **4a** (Scheme 3).[6]



Scheme 3 Intermediates formed during conversion of **1a** into **3a**.

At the outset of our own interest in azadipyrromethenes, an investigation into developing optimised routes to the structural scaffold was carried out starting from 4-nitro-1,3-diarylbutan-1-ones **1a-d**.[7] Routine access to these compounds is available from Michael addition of nitromethane to the diaryl-α,β-unsaturated ketones **8a-d** (chalcones) which in turn are produced by aldol

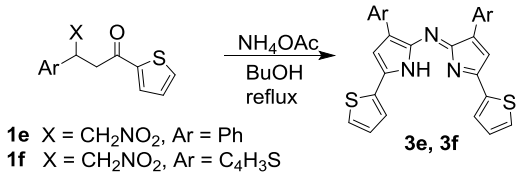
condensation between the corresponding aromatic aldehyde and substituted acetophenone. In the original protocol, harsh (180 °C) solventless conditions were used for the conversion of **1a** into **3a**. By changing the ammonia source from ammonium formate to ammonium acetate, and the use of either EtOH or BuOH as solvents, a general improvement of the reaction yields was obtained. This also had the distinct advantage that the products often crystallize from the reaction and can be purified by simple filtration. Using this approach numerous derivatives have been synthesized (e.g. **3a**-**d**), yields vary with aryl substituent with the better yields typically in the 40-50% range (Scheme 4).[7] As this reaction is formally a starting material dimerization, only two different aryl substituents can be introduced onto **3**.



	Ar^1	Ar^2	yield / %
3a	Ph	Ph	42
3b	Ph	$pOCH_3C_6H_4$	47
3c	$pOCH_3C_6H_4$	Ph	48
3d	$pBrC_6H_4$	Ph	24

Scheme 4 General synthesis of azadipyrromethenes.

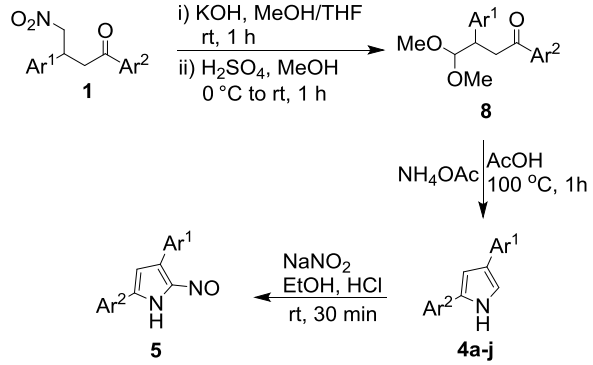
The synthesis of poly-thiophene substituted derivatives has been independently reported via two routes starting from either 4-nitrobutan-1-ones **1e, 1f** or 4-cyanobutan-1-one **2b** (Scheme 5).[8,9] Under the same reaction conditions of NH_4OAc/BuOH at reflux, the yields for di- and tetra-thiophene substituted **3e** and **3f** were low for both routes but marginally higher when **1f** was used as starting substrate (Scheme 5). The use of **2b** as starting substrate suffers from the added disadvantage that KCN is required for its synthesis from the precursor chalcone.[9]



starting material	product	yield / %
1e	**3e**	8-12
1f	**3f**	12
2b	**3f**	5

Scheme 5 Synthesis of thiophene substituted azadipyrromethenes.

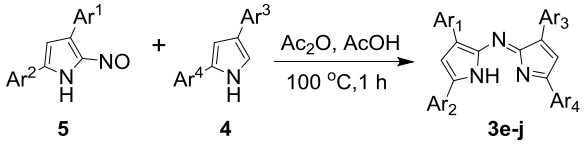
For the development of a general route to non C-2 symmetric azadipyrromethenes bearing up to four different aryl substituents, an efficient route to 2,4-diaryl pyrrole building blocks was required. While alternative literature routes were available to such pyrroles the 4-nitro-1,3-diarylbutan-1-ones **1** were chosen as substrates to allow a common starting material with those utilised for the previously described route as shown in Scheme 4.[10] The crucial step utilised a Nef transformation of **1** into 4,4-dimethoxy-1,3-diaryl-butan-1-ones **8**. Subsequent acetal deprotection and ammonia condensation reaction gave the diaryl pyrroles **4a-j** in good yields. Conversion of pyrroles **4a-j** into α-nitrosopyrroles **5** was readily accomplished by reaction with sodium nitrite in ethanolic HCl (Scheme 6).



	Ar^1	Ar^2	**4** yield /%	**5** yield / %
a	Ph	Ph	70	79
b	Ph	$pMeOC_6H_4$	72	92
c	$pMeOC_6H_4$	Ph	68	86
d	$pBrC_6H_4$	Ph	63	-
e	$pEt_2NCH_2C_6H_4$	Ph	70	-
f	$pO(CH_2CH_2)_2N\text{-}CH_2C_6H_4$	Ph	71	-
g	$pCH_3CONHC_6H_4$	Ph	52	-
h	$pMe_2NC_6H_4$	Ph	52	-
i	Ph	pFC_6H_4	65	83
j	$pEt_2NCH_2C_6H_4$	$pMeOC_6H_4$	59	-

Scheme 6 Pyrrole and nitroso-pyrrole building block synthesis.

Condensation of pyrroles and nitroso pyrroles in acetic anhydride/acetic acid mixture at 100 °C gave azadipyrromethenes such as **3e-j** in good to excellent yields. Typical examples are shown in Scheme **7** illustrating tolerance to a variety of aryl substituents such as halogens, ethers, amines and anilines.[10]

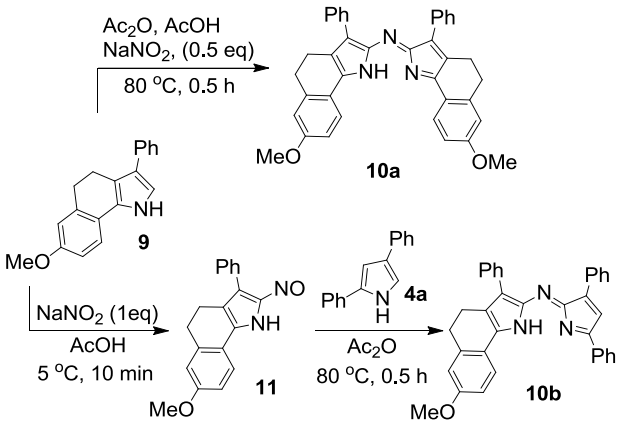


	Ar^1	Ar^2	Ar^3	Ar^4	yield/%
3e	Ph	Ph	$pMe_2NC_6H_4$	Ph	35
3f	Ph	Ph	$pBrC_6H_4$	Ph	92
3g	Ph	Ph	$pEt_2NCH_2C_6H_4$	Ph	94
3h	$pMeOC_6H_4$	Ph	Ph	$pMeOC_6H_4$	72
3i	Ph	pFC_6H_4	$pEt_2NCH_2C_6H_4$	$pMeOC_6H_4$	88
3j	Ph	pFC_6H_4	Ph	$pMeOC_6H_4$	94

Scheme 7 Route to non-symmetric azadipyrromethenes.

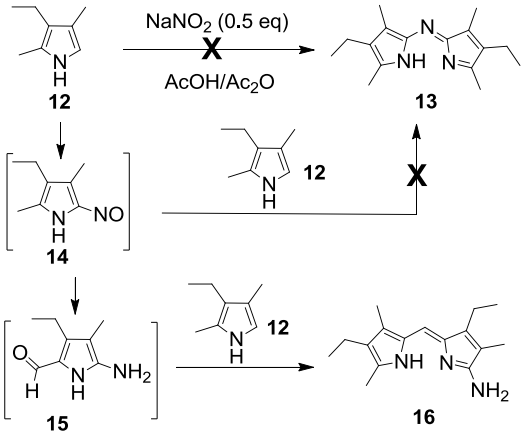
An adaptation of this approach has been reported for producing both symmetric **10a** and non-symmetric **10b** conformationally restricted azadipyrromethenes (Scheme 8).[11-13] Aryl-constrained pyrrole precursors such as **9** were synthesized in four steps with an azirine ring opening being the key step for pyrrole generation. Conversion to aryl ring constrained azadipyrromethene **10a** was achieved, in one pot, by reaction of pyrrole **9** with 0.5 equiv. of

sodium nitrite in acetic acid/acetic anhydride. Different pyrrole subunits could also be incorporated into this one pot approach by first generation of nitrosopyrrole **11** using 1.0 equiv. of sodium nitrite in acetic acid, followed by addition of a second pyrrole **4a** and acetic anhydride (Scheme 8). Attempts to use 2,4-dimethylpyrrole with 2,4-diarylpyrrole for this approach failed to generate the desired azadipyrromethene product, indicating that the 2-aryl pyrrole substituents are necessary for this approach to be successful.[12]



Scheme 8 Synthesis of aryl constrained azadipyrromethenes.

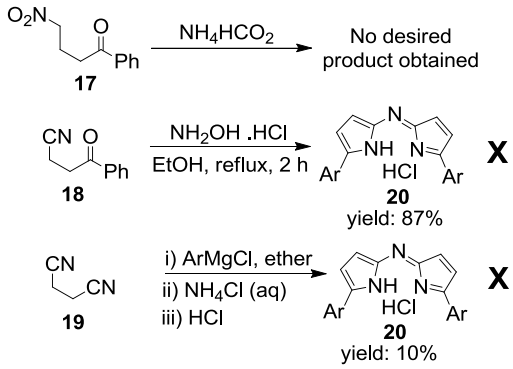
The, as of yet, unresolved roadblock for the synthesis of all alkyl substituted derivatives was highlighted in the attempted synthesis of azadipyrromethene **13** from the reaction of 2,4-dimethyl-3-ethylpyrrole **12** with 0.5 equiv. of $NaNO_2$. Instead of the desired hexa-alkyl-substituted azadipyrromethene **13,** the 5-amino dipyrromethene **16** was the isolated product.[14] The authors



Scheme 9 Unsuccessful attempt for hexa-alkyl substituted derivatives.

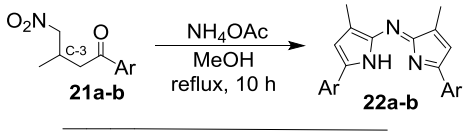
rationalised this unexpected result based on a rapid redox rearrangement of the nitroso-pyrrole **14** to the formyl-amino-pyrrole **15** which subsequently *in situ* condensed with pyrrole **12** to yield dipyrromethene **16**. This unusual rearrangement has been observed by other research teams.[15,16]

In his first report, Rogers attempted to expand the substitution pattern to 5,5'-diaryl derivatives **20** from the reaction of 4-nitro-1-arylbutan-1-one **17** with ammonium formate, but reported that no desired product was formed (Scheme **10**).[2] In 1947, Knott first reported the synthesis of derivatives **20** with positions 3,3' unsubstituted by utilising 4-oxo-4-arylbutanenitrile **18** as starting substrate in reaction with hydroxylamine hydrochloride,[17] a procedure latterly repeated by Boyer *et al*.[18] An additional route to **20** from the addition of aryl Grignard reagents to succinonitrile **19** has also been described (Scheme 10).[19] In 2013, these methods were repeated, but NMR and ES-MS analysis indicated that the structure **20** had been mistakenly assigned in all three of these publications leaving a viable route to **20** yet to be developed.[20]



Scheme 10 Incorrectly claimed syntheses of 3,3' unsubstituted derivatives.

In contrast, synthetic access to 3,3'-dimethyl-5,5'-diaryl derivatives **22** is achievable from 3-methyl-4-nitro-1-phenylbutan-1-one **21** upon reflux with ammonium acetate in alcohol.[20] This is an important approach to obtaining less lipophilic derivatives than the tetraaryl substituted analogues. It is of interest to note that this route is viable with either aryl or alkyl substituents at C-3 (e.g. **1** and **21**) but, as of yet, not when this position is unsubstituted as in **17**. To date, the synthesis of 3,3'-dimethyl derivatives via a pyrrole / nitrosopyrrole condensation route has not been reported.

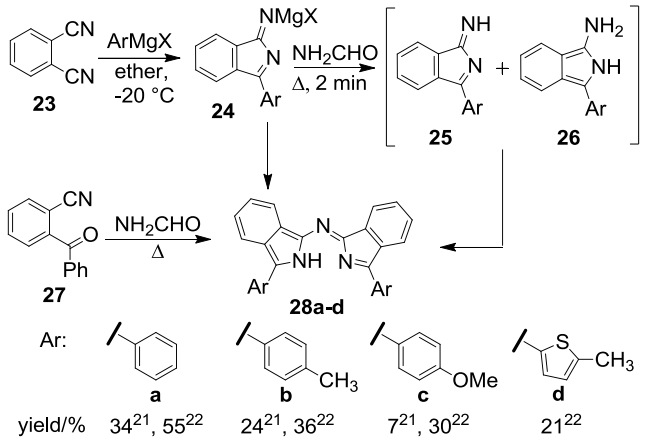


product	Ar	yield / %
22a	Ph	19
22b	*p*$OCH_3C_6H_4$	28

Scheme 11 Synthesis of 3,3'-dimethyl substituted derivatives.

In 1972 Vollman synthesized the benzo fused azadipyrromethenes (3-aryl-*N*-(3-aryl-isoindol-1-ylidene)-isoindol-1-amines) **28a-d** starting from phthalonitrile **23** and 2.5 equiv. of an aryl-Grignard reagent with products isolated by steam distillation (Scheme 12).[21] Alternatively, the product could be obtained by reacting 2-cyanobenzophenone **27** with formamide, but in this case the yield was lower at 10%.[21] More recently, Riede and co-workers optimized these conditions and suggested a plausible mechanism for the formation of the azadiisoindolynmethane (Scheme 12).[22] The optimal conditions found were the addition of 1 equiv. of aryl Grignard reagent to phthalonitrile **23** in diethyl ether at -20 °C thereby generating the magnesium salt of 1-arylisoindoylimines **24**. Evaporation of diethyl ether and subsequent heating with formamide at reflux gave the chromophore products **28a-d**. The

latter step most likely proceeds via the two intermediates **25** and **26** that undergo condensation with formation of the final products (Scheme 12).[22] Numerous other examples of benzo and naphthalene substituted azadipyrromethenes have been reported in the literature utilizing these methods.[23,24]

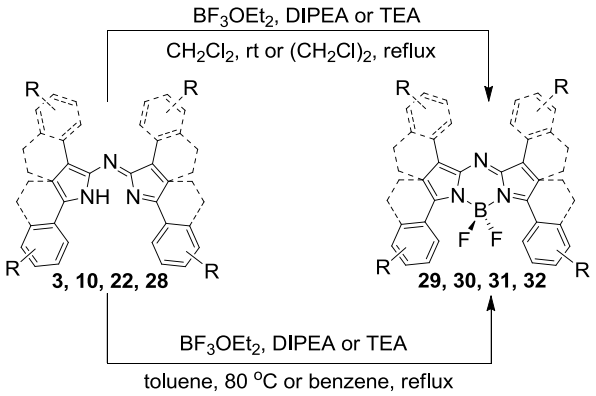


Scheme 12 Routes to benzo fused azadipyrromethenes.

Related asymmetric donor-π-aceptor benzo fused azadipyrromethenes have been generated by reaction of phthalonitriles alone in *t*BuOK-DMF.[25] This unique reaction sequence involved the incorporation of three molecules of phthalonitrile substrate into the final product.

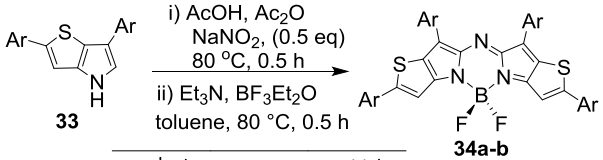
3 Synthetic Elaboration of Azadipyrromethenes

The most common azadipyrromethene derivatization is the formation of their BF_2 chelates, thereby generating a central 5-6-5 fused ring system. This provides structural rigidity to the molecule and inhibits rotation around the C-N pyrrole bridging bonds. The most important impact of this derivatization is that the boron chelate is fluorescent whereas the azadipyrromethene itself is not. The most common synthetic approach to these BF_2 chelates is to use BF_3OEt_2 with a weak organic base such as triethylamine (TEA)[11,24] or diisopropylethylamine (DIPEA)[7,26] in CH_2Cl_2 at rt or $(CH_2Cl)_2$ at reflux (Scheme 13). Alternative conditions, such as toluene at 80 °C[18] or benzene at reflux[23,24], have been reported but often giving lower yields.



Scheme 13 Synthesis of BF_2-azadipyrromethene.

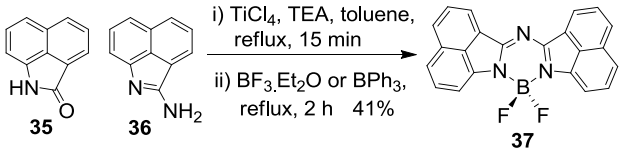
Often the BF_2 chelation step is sufficiently robust to be combined, with the preceding azadipyrromethene forming step, into a one-pot method. In this approach *in situ* chelation is performed following the formation of the azadipyrromethene without prior purification. This method has been reported for some tetraaryl **3**[9] and conformationally restricted **10**[11] derivatives and was adopted for the synthesis of β-thiophene-fused BF_2-azadipyrromethenes **34** (Scheme 14). In this case, reaction of the diaryl-thieno[3,2-b]pyrroles **33** with 0.5 equiv. sodium nitrite in acetic acid/acetic anhydride resulted in the precipitation of the azadipyrromethene, which after filtration was used directly for the chelation step with $BF_3.Et_2O$/TEA in toluene to give the target fluorophores **34a,b** with yields of 54 and 58% respectively.[27]



product	Ar	yield / %
34a	$pOMeC_6H_4$	54
34b	$p^tBuC_6H_4$	58

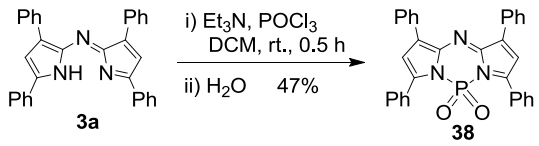
Scheme 14 β-Thiophene-fused BF_2-azadipyrromethenes.

A one-pot synthesis of BF_2 chelated benzo[c,d]indole containing azadipyrromethene **37** has been elegantly achieved by the $TiCl_4$ catalysed condensation of lactam **35** and benzo[c,d]indole-2-amine **36** in toluene followed by treatment with BF_3 etherate.[28]



Scheme 15 One-pot synthesis of benzo[c,d]indole containing azadipyrromethenes.

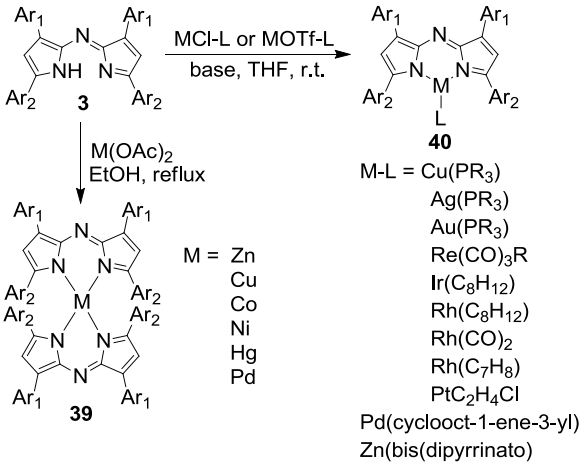
The first example of a PO_2 chelate phosphorusdioxide-azadipyrromethene **38** was synthesized by reaction of azadipyrromethene **3a** with $POCl_3$ in the presence of Et_3N, followed by aqueous hydrolysis (Scheme 16).[29] This sole example illustrates that the synthesis (and properties) of a broad range of other non-metal and metalloid chelates remains to be explored.



Scheme 16 Synthesis of phosphorus-azadipyrromethene **38**.

In Rogers' 1943 publication the zinc, copper, nickel and cobalt metal complexes of **3a** were synthesized from reflux with the corresponding metal acetate (Scheme 17).[1] Specifically the homoleptic copper complex of **39** (M = Cu) was noted as having "excellent light fastness, being equal to Prussian-blue". More recently these complexes have been fully characterised[30] and the

diversity of homoleptic metal chelates has expanded to include Hg[31] and Pd[32]. Metal chelation conditions for Co, Ni, and Zn were well tolerated by phenylacetylene functionalized azadipyrromethenes (at the β-pyrrole positions), providing access to unique photovoltaic constructs.[33,34] The synthesis of homoleptic Cu complexes of benzo fused azadipyrromethenes was first reported by Vollman in 1972 and more recently the range of complexes has been expanded to include Co, Ni, Cu, Zn and Hg derivatives of benzo fused azadipyrromethene **28a**.[21,35]

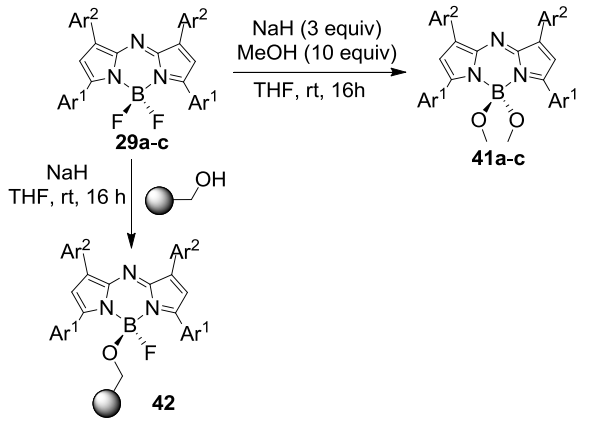


Scheme 17 Synthesis of homo- and hetero-leptic metal complexes of azadipyrromethenes.

To date, nine different metals including Cu, Ag, Au, Re, Ir, Rh, Pt, Pd and Zn have been incorporated into heteroleptic metal complexes **40,** with a variety of associated ligands and comprehensively characterized (Scheme 17).[36-46] Typically, complexes are formed under mild rt conditions in THF with *t*-butoxide or DIPEA as base. This points to an ever expanding future for these complexes not just for their own inherent properties but also for catalysis and material applications.

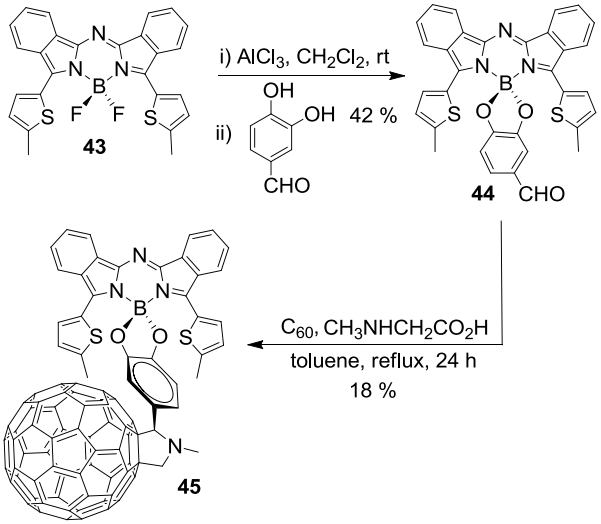
3.1 Derivatization *via* fluorine displacement

In an effort to expand the range of boron complexes, several methods for the nucleophilic displacement of fluorine from the BF_2 chelated azadipyrromethenes have been documented. The first were $B(OR)_2$ derivatives **41a-c**, which were synthesized from precursors **29** by treatment with sodium methoxide at rt (Scheme 18).[47] This transformation was exploited for the covalent linking of **29** to alcohol functionalized particles via a B-O bond, resulting in fluorescent particles and on-bead sensors **42**. The use of an oxygen/fluorine displacement has been exploited for the synthesis of several fullerene–azadipyrromethene conjugates (Scheme 19).[48-51] For example, rt reaction of BF_2 chelated **43** with $AlCl_3$ and 3,4-dihydroxybenzaldehyde generated the benzo-dioxaborole ring substituted product **44** by sequential inter- and intra-molecular fluorine displacements. Reaction of **44** with C_{60} and sarcosine in toluene under reflux gave the fullerene dyad **45**.[52]



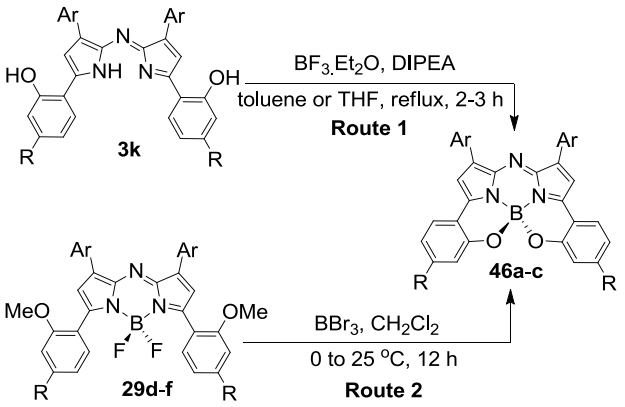
	Ar^1	Ar^2	yield / %
41a	Ph	Ph	65
41b	$pCH_3OC_6H_4$	Ph	60
41c	Ph	$p(CH_3)_2NC_6H_4$	30

Scheme 18 Synthesis of $B(OMe)_2$ chelates.



Scheme 19 Synthesis of fullerene conjugates.

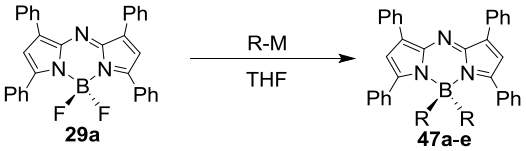
An intramolecular variant of this reaction has allowed access to the helical chiral derivatives **46** which contains an expanded benzo fused 6-5-6-5-6 ring system (Scheme 20). Two synthetic approaches have been developed to this target, one in which the bis-phenol substituted azadipyrromethenes **3k** are reacted with $BF_3.OEt_2$ / DIPEA in toluene or THF at reflux to form the BF_2 chelate followed by *in situ* double intramolecular phenolic oxygen fluorine displacement, thereby generating the structurally constraining benzo(1,3,2)oxazaborinine rings. Alternatively, the bis-aryl methoxy substituted BF_2 chelated precursors **29** could be treated with BBr_3 to demethylate both methoxy groups with *in situ* fluorine displacement by the phenolic oxygens (Scheme 20).[53]



	46a	46b	46c
Ar =	Ph	*p*BrC$_6$H$_4$	Ph
R =	H	H	OMe
% Yield (route 1)	86	n/a	70
% Yield (route 2)	62	36	n/a

Scheme 20 Intramolecular fluorine displacement.

Fluoride displacement with aryl and alkynyl carbon nucleophiles has been accomplished utilizing organolithium and Grignard reagents, allowing for further structural elaboration and refinement of properties (Scheme 21). The method successfully produces boron-aryl and -alkynyl substituted derivatives **47a-d** in moderate yields from **29a** by nucleophilic substitution with the appropriate organometallic reagent.[54,55] F-Displacement with aliphatic nucleophiles are yet to be reported, but the synthesis of the aliphatic dibutylboron B(Bu)$_2$ derivative **47e** has been achieved from the unchelated azadipyrromethene **3a** by treatment with dibutylborontriflate/ trimethylamine in CH_2Cl_2.[55]

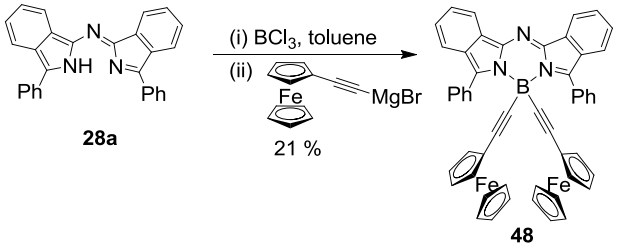


	R	M	yield / %
47a	Ph	MgBr	75
47b	≡—SiMe$_3$	Li	18
47c	≡—Ph	MgBr	68
47d	=	MgBr	53
47e	Bu	---	88*

* Synthesized from azadipyrromethene **3a**

Scheme 21 Fluorine displacement with C-nucleophiles.

Synthesis of the ferroceneacetyleneboryl complex **48** has been achieved from a one-pot two-step procedure. Reaction of azadiisoindolynmethane **28a** with borontrichloride in toluene generated the BCl_2 chelate which was not isolated but converted *in situ* to **48** by reaction with an alkynyl-ferrocence Grignard in an overall 21% yield (Scheme 22).[56]

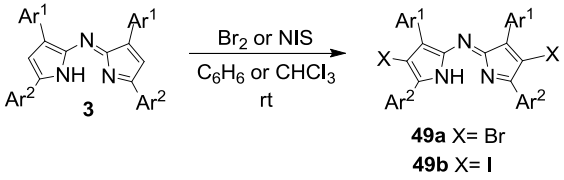


Scheme 22 Ferrocene-azadipyrromethene triad.

3.2 Functionalization at the β-pyrrole positions

3.2.1 Halogenation

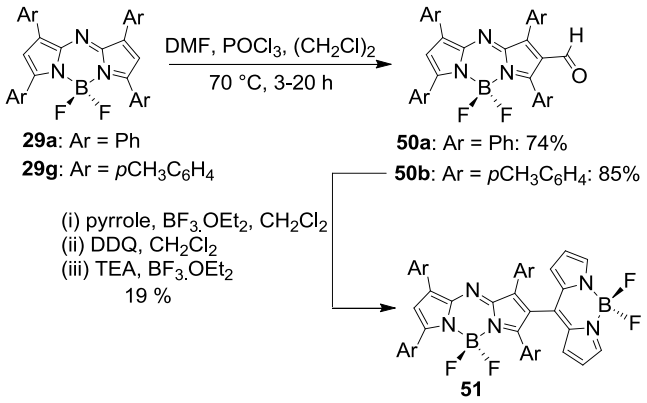
Azadipyrromethenes are susceptible to electrophilic substitution at the C-2 and 6 positions (β-pyrrole positions). The chemical derivatization of the pyrrole rings of azadipyrromethene is a powerful tool to tailor their application based properties. For example, the introduction of heavy atoms such as bromine and iodine on the molecular skeleton dramatically alters the excited state populations, changing the application profile from fluorophore to photosensitizer. As a photosensitizer, **49** can efficiently generate singlet oxygen and thus act as highly effective photodynamic therapeutic agents.[7,57-63] The same halogens could also be useful for activating the molecule for further functionalization via cross-coupling chemistries. Bromination of both pyrrole rings can be routinely performed at rt utilizing Br_2 giving the corresponding dibrominated derivatives **49a** in high yields.[7] In a similar manner, di-iodination is achievable using *N*-iodosuccinimide as iodine source.[64] Subsequent conversion of the halogenated derivatives to their BF_2 chelates can be carried out under the conditions as outlined in Scheme 13.[7] Mono bromination of one β-pyrrole position has also been reported.[65]



Scheme 23 Synthesis of dibromo- or diiodo-azadipyrromethenes.

3.2.2 Formylation

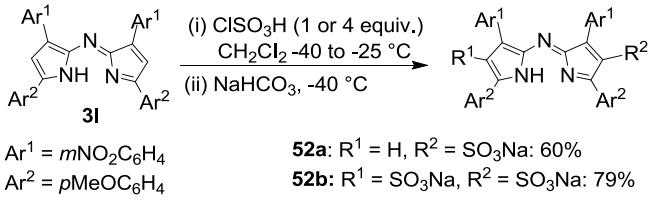
Jiao and co-workers have explored the applicability of the Vilsmeier-Haack formylation for the BF_2-azadipyrromethene **29a** (Scheme 24).[66] Reaction of **29a** with the Vilsmeier reagent (generated *in situ* from DMF and $POCl_3$) at 70 °C for 20 h gave a good yield of the aldehyde product **50**. This electrophilic substitution is selective to the β-pyrrole position with only mono-formyl derivative **50** produced, presumably due to the electron withdrawing effect of the introduced aldehyde substituent. Under similar conditions, **29g** was formylated and aldehyde **50b** converted to the azadipyrromethene-BODIPY dyad **51** (Scheme 24).[67] This reaction sequence is a good illustration of the complexity of sequential transformations that can be carried out on azadipyrromethenes.



Scheme 24 Formylation of azadipyrromethenes.

3.2.3 Sulfonation

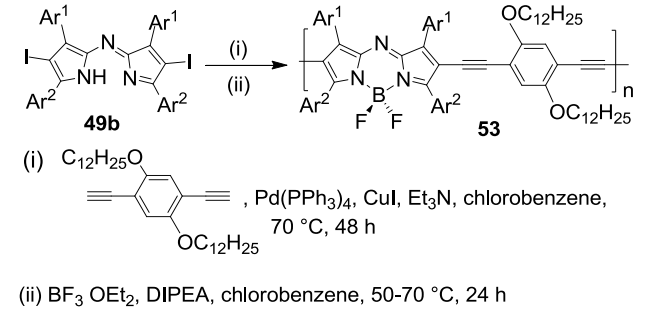
Mono- or di-sulfonation of azadipyrromethene **3l** was achieved with the appropriate equivalence of chlorosulfonic acid in CH_2Cl_2 at low temperatures (Scheme 25). Disappointingly, BF_2 chelation of sulfonated **52a** and **b** failed under a variety of conditions. An alternative approach of reacting the BF_2 chelated version of **3l** also failed to give the desired product due to loss of the BF_2 fragment during the reaction. This instability was attributed to the electron deficient character of the BF_2 chelated **3l**.[68]



Scheme 25 Mono and di-sulfonation.

3.2.4 Metal mediated coupling reactions

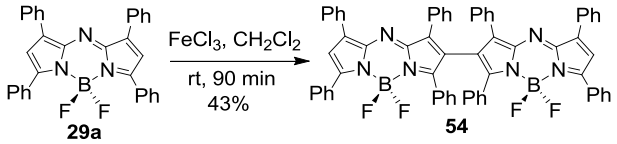
Azadipyrromethenes with halogen substituents on the β-pyrrole positions have been utilised to form conjugated oligomers *via* Sonogashira cross-coupling reactions (Scheme 26). For example, Pd/Cu catalyzed reaction of iodo azadipyrromethenes **49b** and 1,4-bis-(dodecyloxy)-2,5-diethynylbenzene followed by BF_2 chelation gave oligomers **53**.[64] Highest molecular weight oligomers were obtained when Ar^1 and Ar^2 were *para*-substituted with *t*Bu groups to aid solubility. The Pd catalysed Suzuki-Miyaura cross coupling of



Scheme 26 Azadipyrromethene conjugated oligomers.

dibrominated derivative **49b** (Ar^1 = *p*-$CH_3OC_6H_4$, Ar^2 = Ph) with aryl boronic acids generated hexaarylated azadipyrromethenes in moderate yields (25-35%).[69]

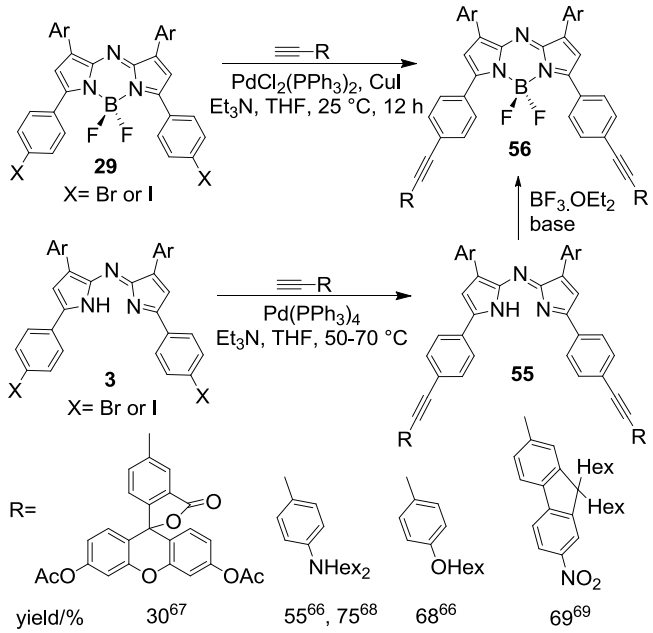
The room temperature oxidative homocoupling with $FeCl_3$ is a protocol for the facile dimerization of BF_2-aza-dipyrromethene to produce **54** as reported by Bard *et al* (Scheme 27).[70] The coupling takes place in the β-pyrrole position with no need for a previous functionalization with an activating group. It is of interest to note that the reaction did not proceed to form polymer or higher oligomeric products.



Scheme 27 Fe mediated homocoupling.

3.2.5 Functionalization at the aryl rings

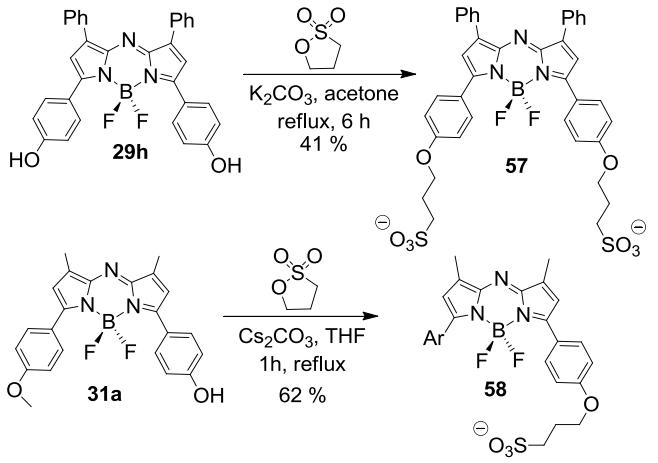
For specific applications it is attractive to extend the π-conjugation of the azadipyrromethene system and the route of choice to achieve this is via Sonogashira coupling of bromo or iodo substituted aryl rings (Scheme 28). This has been described for both tetraaryl azadipyrromethene **3**, their BF_2 chelates **29** and zinc complexes.[71-75] Representative examples and conditions are shown in Scheme 28. This versatile approach has been exploited to substitute with ethynyl-(hexyloxy)-benzene[71], ethynyl fluorescein diacetate[72], ethynyl-*N*,*N*-dihexylaniline[71,73] and ethynyl nitrofluorene[74] groups to produce the constructs **56**. Following alkynyl coupling with azadipyrromethenes **3**, BF_2 chelation of the products **55** was possible under typical chelating conditions (Scheme 28). Suzuki-Miyaura cross coupling of dibrominated derivative **29** has also been reported for a range of aryl boronic acids.[76]



Scheme 28 Extending π-conjugation.

Aryl functionalization for aqueous solubility

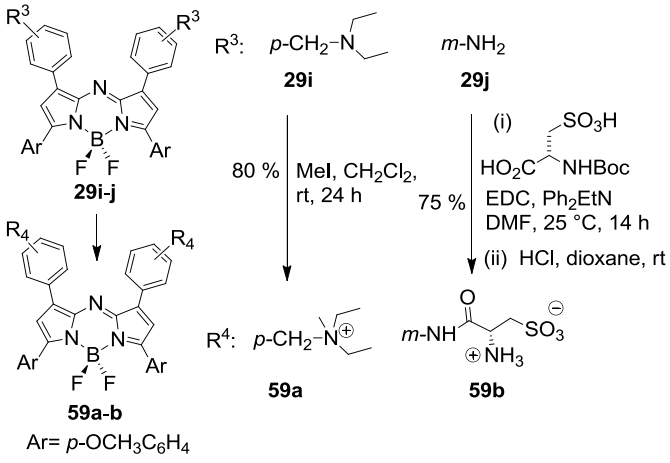
The inclusion of phenol substituents on the azadipyrromethene extends the possibilities for further functionalization via ether bond formation (Scheme 29). One strategy adopted to increase the



Scheme 29 Aqueous soluble derivatives.

aqueous solubility of BF_2-aza-dipyrromethenes is the introduction of water-solubilizing functional groups via phenolic oxygen(s). Examples of this include bis- and mono-alkyl sulfonic acid derivatives **57** and **58** which are formed by reaction of **29h** or **31a** with propane-1,3-sultone (Scheme 29).[77,20] Both derivatives show good aqueous solubility and the ability to be uptaken into cells without need for formulation or delivery agents.

Ammonium salts and cysteic acid derivatives have also been employed to enhance aqueous solubility (Scheme 30). The bis-ammonium salt derivative **59a** was generated from the reaction of **29i** with methyl iodide in dichloromethane.[77] Ethyl(dimethylaminopropyl)carbodiimide (EDC) coupling of the *meta*-amino substituted **29j** gave the di-cysteic acid derivative **59b** which showed significantly enhanced hydrophilicity.[68]

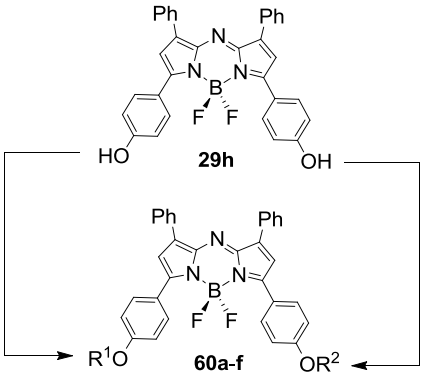


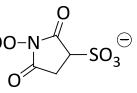
Scheme 30 Improving aqueous solubility.

The use of clinical formulations as an alternative strategy to synthetic modification has also been employed to obtain stable aqueous solutions of fluorescent and singlet oxygen producing azadipyrromethenes allowing for their use *in vitro* and *in vivo.*[7, 58, 61]

Fluorochromes and material conjugations

Functionalization with aqueous solubilizing groups has formed one part of the strategies for the synthesis of several fluorochromes, i.e. fluorophores capable of bio-conjugations. For this synthesis one phenolic ring is substituted with a water solubilizing group and the other with a spacer and reactive functional group through which the covalent conjugation can be achieved (Scheme 31). Examples of conjugating functional groups incorporated by this approach include alkyne **60a**[78], **60b**[79], azide **60c**[80], activated ester **60d**[81], and maleimide **60e**[82].

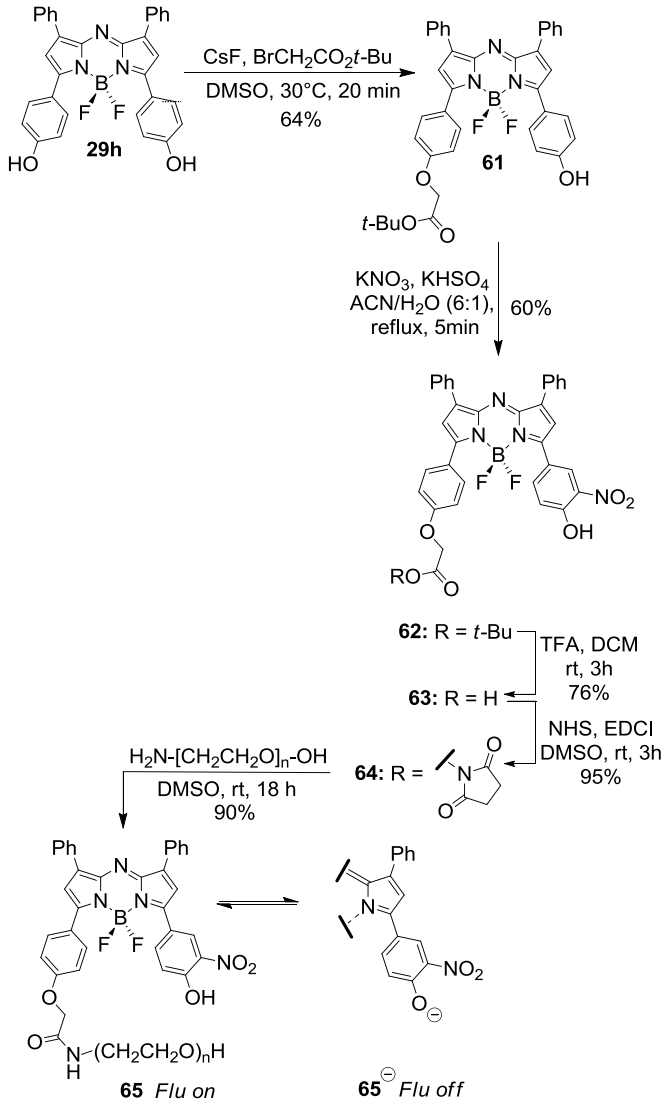


	R^1	R^2
60a	H	$H_2C-C\equiv CH$
60b	$H_2C-C\equiv CH$	$OC(O)OCH_2CH_2SSCH_2CH_2OH$
60c	$CH_2CH_2CH_2SO_3^{\ominus}$	$CH_2C(O)NHCH_2CH_2(OCH_2CH_2)_3N_3$
60d	$(CH_2CH_2O)_3CH_3$	$CH_2CH_2NHCOCH_2CH_2COO-$ 
60e	$CH_2CH_2CH_2SO_3^{\ominus}$	$CH_2CH_2NHCOCH_2CH_2-$ 

Scheme 31 Azadipyromethene fluorochromes.

In our own work we have utilized a multi-step synthesis to produce the bio-responsive NIR-fluorophore **65** which offers significant potential for use in live cellular and *in vivo* imaging.[83] Emission from the probe was shown to be highly selective for cellular lysosomes, capable of real-time continuous cellular imaging of fundamental cellular processes, and allowed for direct translation to *in vivo* tumour imaging. The starting point of the synthesis was the BF_2-chelated bis-phenol azadipyrromethene **29h**, which was mono-alkylated with *t*-butyl bromoacetate to produce **61**. A key step of the synthetic sequence was an *ortho*-nitration of **61** with $KHSO_4/KNO_3$ producing **62** which fine-tuned the fluorescent switching properties of the fluorophore. Following *t*-butyl ester hydrolysis to **63** and conversion to the activated ester fluorochrome **64** by reaction with *N*-hydroxysuccinimide and *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide (EDCI), a terminal amine functionalized polyethylene glycol polymer was conjugated to make the final aqueous soluble bio-responsive NIR-fluorescent imaging agent **65** (Scheme 32).[83] This route is an encouraging

illustration of the level of synthetic complexity that is achievable with the azadipyrromethene scaffold.



Scheme 32 Bio-responsive NIR-fluorescent azadipyrromethene.

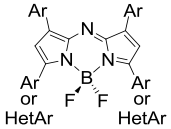
The bis-phenolic substituted derivative **29h** has also been elegantly employed as starting point for the synthesis of several dyad and triad donor acceptor materials, by coupling with BODIPY[84,85], Zn-tetraarylporphyrin[85,86], Zn-phthalocyanine[87], and subphthalocyanines.[88]

Complementary to synthetic routes, extensive time-dependent density functional theory (TD-DFT) calculations have been utilised to gain understanding of the structural effects on electronic structure and predict the important photophysical characteristics of this chromophore class.[89-97]

Conclusions

Since the turn of the century research interest in azadipyrromethenes has blossomed. Several strategies now exist to synthesize this important nitrogen linked bi-pyrrolic scaffold, and numerous approaches have been developed that allow structural modification post-synthesis. The key advantage of being readily able to adapt the functionality about the azadipyrromethene core has allowed for the properties of the final azadipyrromethene to be application specifically tailored. In the following tables these applications have been grouped as excited state properties (Table 1), NIR-optical sensors (Table 2), bio- and material-conjugates (Table 3), photodynamic therapy and photoredox catalysts (Table 4), solar energy materials (Table 5), and optoelectronic materials (Table 6). At this still early developmental stage of the azadipyrromethene scaffold, the future looks very promising for translation from research laboratory to real-world medical and/or material function with more leading edge applications and uses to emerge. This seems fitting, as it was traditional dye chemistry which laid the foundations for modern industrial chemistry and currently it can still be found as the basis of emerging 21st century technologies.

Table 1. Excited State Properties

Entry	Structure	Substituent	Abs / nm	Flu / nm	Comments	Ref.
1		aryl derivatives	647-716	669-750	Φ_f = 0.23-0.36 ε = 78-85,000 $M^{-1}cm^{-1}$ high photostability Φ_{deg} <x10^{-8} , flu. lifetime 2.2 ns, transient absorption properties aqueous soluble derivatives conformationally restricted derivatives Φ_f = 0.26-0.81	7, 26, 98 60 77, 68 99 100

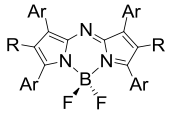
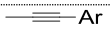
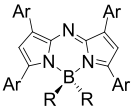
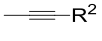
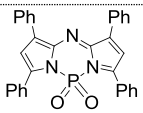
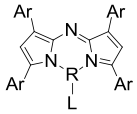
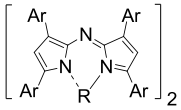
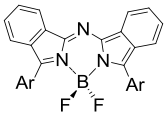
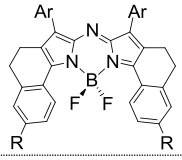
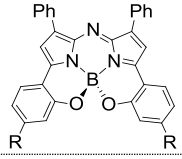
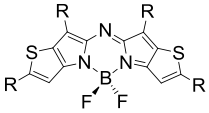
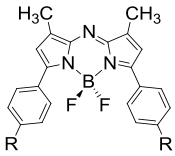
		heteroaryl derivatives	710-727	732-751	Φ_f = 0.44-0.46 ε = 108 - 120,000 $M^{-1}cm^{-1}$ fluorescence lifetime: 2.2-3.5 ns	8, 9
2		R = Br, I	645-702	666-732	ε = 64-82,000 $M^{-1}cm^{-1}$. Φ_f = 0.01-0.22; $\Phi^1{}_{O_2}$ = 0.74 triplet quantum yield Φ_t = 0.72 photo degradation Φ_{deg} = 5.4x10^{-8} flu. lifetime:550 ps - 1.6 µs	7, 26, 59, 65 60, 63
		R = H, CHO	624	663	Φ_f = 0.45 ε = 53,703 $M^{-1}cm^{-1}$	66
		R = Ar	653-656	688-750	Φ_f = ≤0.01-0.05 ε = 50-83,000 $M^{-1}cm^{-1}$ flu. lifetime 0.06-0.26 ns	69
		R = 	716-813	negligible		64
3		OMe	620-733	674-822	Φ_f = 0.30-0.31 ε = 51-76,000 $M^{-1}cm^{-1}$	47
		Ar	618	662-666	Φ_f = 0.018-0.027 ε = 50-53,000 $M^{-1}cm^{-1}$	54
		-C=CH 	642-647	670-671	Φ_f = 0.16-0.29 ε = 51-87,000 $M^{-1}cm^{-1}$ flu. lifetime = 1.48 ns	54, 55
4		--	625	661	Φ_f = 0.08 ε = 33,000 $M^{-1}cm^{-1}$	29
5		Cu, Ag, Au	597-631	642-667	Φ_f = 0.0021-0.012 ε = 28-69,000 $M^{-1}cm^{-1}$	37, 36
6		Zn, Cu, Co, Ni, Hg, Pd	562-642	Non-fluorescent	ε = 55-90,000 $M^{-1}cm^{-1}$	30, 31, 32, 101, 102
7		--	681-794	723-841	Φ_f = 0.01-0.30 ε = 35,800-174,000 $M^{-1}cm^{-1}$ solid state emitters	22, 23, 24,103, 104
8			539	541	Φ_f = 0.08-0.60 ε = 48,000 $M^{-1}cm^{-1}$ Flu. lifetime = 5.0 ns	28
9		H OCH_3	705 721-746	718 732-780	Φ_f = 0.28-0.31 ε = 157-162,000 $M^{-1}cm^{-1}$	13, 11, 12, 105
10		H OCH_3	728 765	746 782	Φ_f = 0.18-0.51 ε = 73-80,000 $M^{-1}cm^{-1}$ helical chiral fluorophore	53 106, 107
11		*p*-$MeOC_6H_4$ *p*-*t*BuC_6H_4	788 767	814 793	Φ_f = 0.10-0.12 ε = 170,000-223,900 $M^{-1}cm^{-1}$ high photostability flu. lifetime = 1.18-1.69 ns	27
12		H OCH_3	618 648	642 678	Φ_f = 0.41-0.44 ε = 64-81,000 $M^{-1}cm^{-1}$ aqueous soluble derivatives	20

Table 2. NIR Optical Sensors

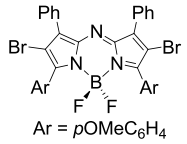
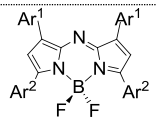
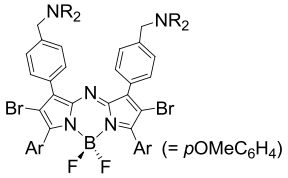
Entry	Analyte	Receptor Used	Response Range	Comments	Ref.
1	pH	benzylamine	4.9-9 and 3-7	microenvironment polarity responsive *in vitro* cellular imaging in MDA-MB-435 cells library of sensors studied	108 109 110
2		amine + phenol	3-8	*in vitro* and *in vivo* fluorescence imaging and super-resolution sub-diffraction imaging	111
3		aniline	0.5-2	low response to microenvironment polarity ratiometric fluorescence	112
4		aniline	1-3 and 3-6M HCl	triple absorption and emission responsive sensor	113
5		conformationally restricted aniline	1.0-4.0	microenvironment polarity responsive	114
6		phenol	6-8	alkyne substituted for azide conjugation	78
7		phenol	6-8	immobilized in a polyurethane hydrogel D4 film upon the polystyrene layer	115
8		phenol	6.52-10.75	live cell imaging and *in vivo* bio-distribution	116
9		phenol	6-9	conjugated with carbon nano-onions, *in vitro* imaging in HeLa Kyoto cells	117
10		phenol	5-7	as part of block co-polymer micelles consisting of poly(methacrylic acid)-block-poly(poly(ethylene glycol) methyl ether methacrylate) micelles loaded with doxorubicin with intracellular pH promoted release of drug and NIR-fluorescence response	118
11		*o*-nitrophenol	4-6	emission from the probe highly selective for cellular lysosomes and capable of real-time continuous imaging of endocytosis, lysosomal trafficking and efflux in 4D mouse model *in vivo* tumour imaging demonstrated using an MDA-MB-231 subcutaneous tumor model	83
12		*o*-chlorophenol	5.8-8.6	hydrogel entrapped/pH inside coral polyps	119 120
13		phenol	4-8	SWNT-conjugate.	121
14		hydroquinone to quinone	4.0-8.0	*in vitro* cell and *in vivo* tumor imaging	122
15		piperidine	4-7	applied to pH measurement in blood samples also metal ion responsive	123
16	CO_2	di-phenol	0.1-98.1 kPa CO_2	demonstrated by monitoring carbon dioxide production and consumption of a Hebe plant also pH-sensitive indicator dyes	124
17	Na^+, K^+	pyridine macrocycle		imaged in normal cells (MCF-10A, HL7702) and cancer cells (MCF-7, HepG2).	125
18	Hg(II)	pyridyl	C(Hg(II)) = 0 - 8 µM	Cu(II) and Zn(II) show minor responses	126
19		thienyl	C(Hg(II)) = 0 - 10 µM	fluorometric and colorimetric responses	127
20	H_2S	azido	C(H_2S) = 0 - 40 µM	detection and analysis of H_2S in the aqueous medium	128
21	H_2S_n	*p*-nitrofluoro benzoate	C(Na_2S_2) = 0 - 20 µM	living cells (RAW264.7 cells) and *in vivo* (BALB/c mice) imaging	129, 130
22	NO	amino	C(NO) = 5 - 200 nM	detection and analysis of NO in the aqueous medium	128
23	F^-	silicon	C(F^-) = 0 - 20 µM	F^- monitoring in living HeLa cells	131
24		triarylborane	detection limit of C(F^-) = 0.1 ppm	good selectivity over Cl^-, CN^-, NO_3^-, ClO_4^- and $H_2PO_4^-$	132
25		B-Se Ar bond cleavage	detection limit of C(F^-)= 7.4×10^{-8} mol/L	fluorescent imaging of HepG2 cells	133
26	NH_4^+	pyrazine	C(NH_4^+) = 0 - 1.0 mM	colorimetric naked-eye detection	134
27	HNO	diphenylphosphino benzoyl	C(Angeli's salt) = 0 - 10 µM	detection in RAW264.7 cells and *in vivo* mouse model	135, 136
28	NO_2^-	aniline	detection limit of C(NO_2^-) = 20ppb	detection in aqueous media	137
29	glucose	aryl boronic acid groups	C(glucose) = 60 µM – 100 mM	detection in diluted whole blood samples	138
30	saxitoxin	18-crown-6 crown ether	C(STX) = 0 - 20 µM	binding constant $3\text{-}9\times10^5$ M^{-1}	139

31	cysteine	cleavage of 2,4-dinitrobenzene-sulfonyl group	detection limit of C(cysteine) = 5×10^{-7} M	2,4-dinitrobenzene sulfonyl (DNBS) group quenches excited state via PET, following thiol cleavage of DNBS fluorescence signal is established	140
32	Cu(II)	2-picolinic ester	-	ratiometric photoacoustic imaging probe	141
33	CN^-	BF_2-azadipyrromethene	detection limit of 8.6×10^{-7} M	chemodosimetric, colorimetric and fluorescence sensor addition of cyanide to pyrrole ring causes new emission band at 600 nm	142

Table 3. Bio- and Material-Conjugates

Entry	Conjugating Functional Group	Covalently Attached Group	Comments	Ref.
1	alkyne	galactose	alkyne-azide cycloaddition, imaging in MDA-MB-231 cells, bio-conjugatable and pH responsive	78
2	alkyne	cancer cell-directing biotin unit	linked with anti-cancer drug gemcitabine via disulphide bond and alkyne-azide cycloaddition conjugating biotin used to monitor drug delivery and cellular imaging in cells	79
3	alkyne	four PEG chains	increased water solubility	143
4	alkyne	β-cyclodextrin	host guest complexes with tetra-sulfonated porphyrins	144
5	activated ester	*N*-Boc-lysine, 14.4 kDa protein lysozyme, 23.3 kDa protein trypsin	representative amine conjugations with amino acid lysine and proteins lysozyme and trypsin	78
6	azide	alkyne-substituted mono- and di-saccharides	alkyne-azide cycloaddition conjugate imaging shown in HeLa Kyoto cells	80
7	maleimide	amino acid cysteine tripeptide glutathione, CPP peptide (C(βA)SKKKKTKV-NH_2), cRGD peptide (c[RGDfK(SH)])	maleimide thiol conjugation demonstrate in HeLa Kyoto cells and human esophageal cancer cell line ECA-109	82
8	amine	activated ester functionalised SWNT	donor-acceptor material consisting of BF_2-azadipyrromethenes and highly functionalised single wall carbon nanotubes charge transfer from photo-excited donor to SWNT acceptor, radical ion pair lifetime of 1.2 ns	145
9	amine	activated ester functionalised polystyrene nanoparticles	NIR-fluorescence responsive to micro-environmental change occurring upon cellular uptake allowing real-time live cell imaging.	146

Table 4. Photodynamic Therapy and Photoredox Catalysts

Entry	Structure	Comments	Ref.
1	 Ar = *p*OMeC$_6$H$_4$	synthetic methods described spectroscopic characterization: Φ_f = 0.1; τ_f = 550 ps; Φ_{isc} 0.72; $\Phi^1{}_{O_2}$ = 0.74 nanomolar *in vitro* cellular efficacy for PDT *in vivo* mouse tumour model PDT study *in vivo* mechanism of PDT action shown study of heavy atom positional effects on triplet state population	7, 26 60 57 58 61 147
2		library of 7 derivatives examined for cytotoxicity and cell death pathways	148
3		microenvironment pH responsive singlet oxygen generation, protonation of benzylamine groups inhibits PET excited state quenching and turns on singlet oxygen production via triplet state population nanomolar *in vitro* cellular efficacy shown with PDT in MRC5 cell line	62

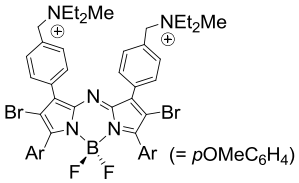
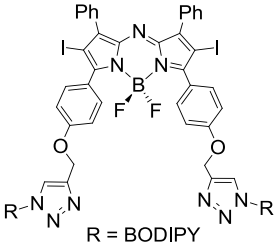
4		antimicrobial photodynamic therapeutic agent rapid 10 min uptake into Gram-positive and -negative bacterial strains broad spectrum pathogen response with Gram-negative bacterium, E. coli and the pathogenic yeast C. albicans between 3.4 – 6.8 log_{10} reductions achievable with 5 μg/mL photosensitizer and 15 J/cm^2 light doses	59
5		photoredox catalyst comprised of broadband visible light absorbing iodo-BF_2-azadipyrromethene-BODIPY triad shown to act as a triplet photosensitizer as photo-catalyst for 1,3-dipolar cycloaddition reactions using tetrahydroisoquiniline and *N*-substituted succinimides as substrate	149150

Table 5. Solar Energy Materials

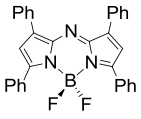
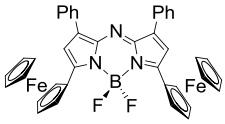
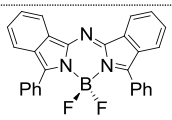
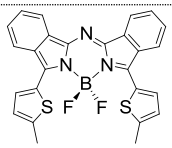
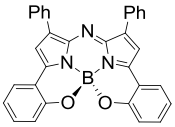
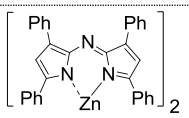
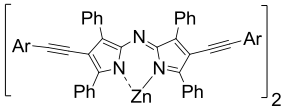
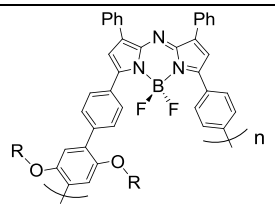
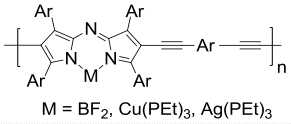
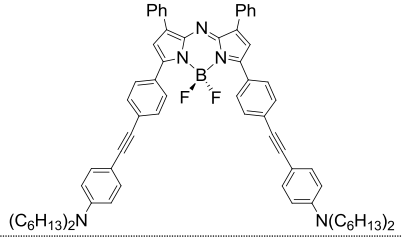
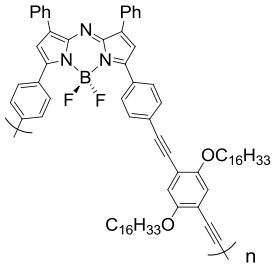
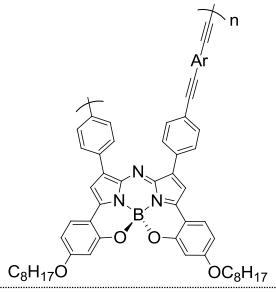
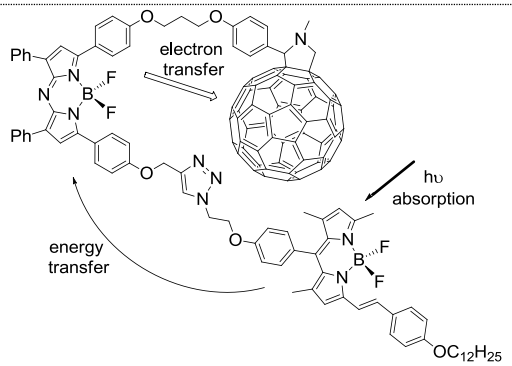
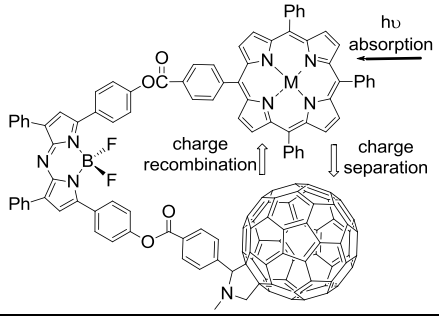
Entry	Structure	Comments	Ref.
1		used as donor in combination with phenyl-C_{60}-butyric acid methyl ester as acceptor power conversion efficiency = 1.2%. V_{OC} of 0.96 V	151
		tetra-alkynes substituted derivative incorporated via click reactions as core acceptor in light harvesting dendritic systems (structure not shown)	152
2		donor acceptor diad of azadipyrromethene and ferrocene, ferrocene units are electronically coupled to each other	153
		molecular clip type structure consisting of ferrocene-azadipyrromethene donor acceptor triad (structure not shown) laser flash photolysis showed with fast and efficient charge separations	154
3		used as donor in combination with phenyl-C_{60}-butyric acid methyl ester as acceptor power conversion efficiency = 1.1% V_{OC} of 0.65 V	151 155
4		used as donor in combination with phenyl-C_{60}-butyric acid methyl ester as acceptor no near-IR photocurrent sensitization	155
5		used as donor in combination with vapour deposited C_{60} acceptor layer power conversion efficiency = 2.63% open circuit voltage (V_{OC}) = 0.8 V improved performance when blended with camphoric anhydride (high dielectric constant molecule)	156 157
6		used as acceptor in combination with poly(3-hexylthiophene) donor power conversion efficiency = 1.32% open circuit voltage (V_{OC}) = 0.82 V	33 34 158
		used as acceptor in combination with poly(3-hexylthiophene) donor power conversion efficiency = 3.9% for R = Ph open circuit voltage (V_{OC}) = 0.76 V for = Ph	

Table 6. Optoelectronics Materials

Entry	Structure	Comments	Ref.

1		π-conjugated polymers for electron transport materials derivatives showed high electron mobility (3.6×10^{-4} $cm^2V^{-1}s^{-1}$) and low threshold voltage (4 V) in electron-only devices with ITO/Ca/polymer/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline/LiF/Al configuration	159
2	 M = BF_2, $Cu(PEt)_3$, $Ag(PEt)_3$	π-conjugated *para*-phenylene ethynylene alternating copolymers for electron transport materials physical properties tuned by BF_2 or metal chelation, BF_2 gave higher electron affinity (4.5 eV) and lower optical bandgaps (<1.34 eV)	160 161
3		utilised in solid state hybrid materials of sol-gel matrix as optical power limiter (OPL) operating in the telecommunication wavelengths broadband OPL performances in NIR region between 1200-1600 nm for related structures and applications see reference	162 163
4		synthesised via Pd catalysed Sonogashira coupling to yield polymer of molecular weight 5,700 with photoluminescence quantum yield of 24% at 753 nm	164
5		three derivatives synthesised with Ar being 2,5-diethynyl-3,4-dimethylthiophene or 3,6-diethynyl-9-octadecyl-carbazole, or 1,4-diethynyl-2,5-bis(octyloxy)benzene. NIR emission over 820 nm, quantum yields 5-9%, and band gaps in the range of 0.99-1.21 eV	165
6		photosynthetic antenna-reaction centre mimic. Upon excitation of the boron-dipyrromethene effective energy transfer to the azadipyrromethene occurs which subsequently transfers an electron to the fullerene photosynthetic antenna-reaction centre mimic. V-configured BODIPY-BF_2-azadipyrromethene-C_{60} triad (structure not shown) showed through bond singlet-singlet energy transfer from BODIPY* to BF_2-azadipyrromethene and through space electron transfer to produce $BODIPY^{\bullet+}$-BF_2-azadipyrromethene- $C_{60}^{\bullet-}$ radical-ion pair as the main photochemical events	166 167
7		as a result of the close proximity of the porphyrin and fullerene the photoinduced charge separation from the singlet excited porphyrin involves fullerene with charge recombination also following this path of through space instead of electron migration from the fullerene anion radical to the covalently linked azadipyrromethene a related V-configured subphthalocyanine-BF_2-azadipyrromethene-C_{60} triad (structure not shown) showed competitive electron transfer leading to the formation of $SubPc^{\bullet+}$- BF_2azadipyrromethene-$C_{60}^{\bullet-}$ and $SubPc^{\bullet+}$-BF_2azadipyrromethene$^{\bullet-}$-C_{60} charge separated states	168 169

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Notes and references

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