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Synthetic Procedures, Properties, and Applications of Thiophene-Based Azo Scaffolds

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Abstract

The thiophene nucleus has been established as the potential entity in heterocyclic chemistry's growing chemical world with promising pharmacological activities. Thiophene-based azo dyes compounds synthesized through different routes bear variable magnitudes of various activities such as textile, food, cosmetic, polymer, leather articles, paints, and ink industries numerous potential applications accredited to the azo function. The double bond linkage between two N atoms is widely found as a chief scaffold in a massive library of organic compounds with promising industrial and biological properties. The knowledge of various synthetic pathways and the diverse physicochemical parameters of such compounds draw the special attention of medicinal chemists to produce a combinatorial library. The present review provides a broad view of the synthesis and properties of compounds with thiophene nuclei. Therefore, it is a significant surge in designing novel azo dyes and introducing advanced synthetic routes for their preparation.

Keywords: Heterocyclic; Thiophene; Regioselective; Azo dyes.
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1. Introduction

Azo compounds have been used for dyes due to their versatile application in various fields such as in coloring for various materials, the dyeing of textile fibers, organic compound synthesis, biological–medical studies, the 2-amino thiophene compound and its benzo analogs are used in intermediates in the dyestuff industry, pharmaceutical applications.[1] Thiophene is derived from the Greek word "phaino" which means shinning. It coexists in hydrocarbons i.e., petroleum or coal. Physically, they are a stable liquid close to the benzene compounds' features (boiling point).[1-2] It is a stable, readily available and their derivative has been a constant matter of investigation.[3] The red to blue colors showed thiophene-based azo dyes with a high extinction coefficient in comparison with aniline-based azo dyes.[1] The combustion heat indicates resonance stabilization to the extent of (22-28 K. Cal/mol.), somewhat less than the benzene resonance energy (36 K. Cal./mol.). As the world's population increases day by day and health problems also expand accordingly, the need to discover new therapeutics is the need of the hour. Chemically, it is analogous to pyrrole, where nitrogen in pyrrole carries a hydrogen atom, and the oxygen or sulfur carries an unshared pair of electrons which is in the sp^2 hybridized orbital. It obeys the Huckel or aromaticity rule ($4n + 2\ \pi$) electron rule (n = 0, 1, 2, and so on) and is considered aromatic. The investigational approaches toward Structure Activity Relationship (SAR) focusing on the search for optimized candidates have become immensely important. It belongs to a class of heterocyclic compounds containing a five-membered ring made up of one sulfur as a heteroatom with the formula C_4H_4S. They occur in coal tar distillate. The discovery of thiophene in coal tar benzene provides one of the classic anecdotes of organic chemistry. It was discovered as a contaminant in benzene. On the above basis, azo dyes are

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usually designed to resist biodegradation under aerobic conditions, the recalcitrance of these compounds being attributed to the presence of sulfonate groups and azo bonds.[4] Azo dyes are the organic compound containing coloring azo function (C-N=N-C) which is surrounded by an aromatic ring along with uniting two symmetrical and/or asymmetrical identical or non-azo alkyl or aryl radicals [5]. Recently, these chemical compounds have received more attention in both scientific and technological fields.[6] They are widely utilized in the synthesis of organic industrial dyes and a broad colour spectrum. They can be classified into mono-azo dyes, diazo dyes, trisazo dyes, and poly-azo dyes[7] but mono-azo compounds account for the great majority of them. They have versatile applications in different fields such as optical data storage, non-linear optics (NLO),[8,9] dye-sensitized solar cells,[10] inkjet printers,[11] metallochromes indicators[12] photochemical materials,[1,13] liquid crystal display,[14] photo-sensitizers,[15] biological-medical studies,[16] and electro-optical devices.[17] In addition, they are used in the synthetic industry, drug, and food industries,[18] and dyeing textile industries such as cotton, silk, wool, and viscose.[16] The design of drug molecules arguably offers some of the greatest hopes for success in the present and future eras. Heterocyclic compounds are widely distributed in nature and are essential for life. There are vast numbers of pharmacologically active heterocyclic compounds which are regularly used clinically.[19] Dyes have the ability to generate strong dye-fiber interaction due to durable functional protection to textiles. The mosquito-repellent and UV-protective acrylic fabric have been synthesized by the novel cationic (basic) dye.[20] Dyes have some useful hi-tech applications such as dye-sensitized solar cells, photochromic, biomedical, photodynamic therapy, treatment of cancer, dye-sensitized solar cells, and fluorescent sensors.[21] A comprehensive summary of the papers on synthesis, properties, and applications of thiophene, and thiophene-based azo dyes are summarized. These applications were found excellent in colored plastics, fabrics, and others, therefore, expected that a comprehensive summary will be helpful in future research to develop more potent multifunctional azo dyes.

2. Properties of thiophene and thiophene-based azo dyes

Thiophene is a colorless liquid at room temperature. Derivates of azo dyes include azo pigment, which is insoluble in water and other solvents. Azo-dyes are solid, most are salts. Aryl-azo compounds have vivid colors mostly red, orange, and yellow due to a consequence of π-delocalization. Methyl orange is used as an acid-base indicator. The mostly colored component is the anion but some azo-dyes are cationic also. The anionic dyes arise from the presence of 1-3 sulphonic acid groups, which are fully ionized at the pH of the dyed article:

$$RSO_3H \rightarrow RSO_3^- + H^+ \quad (1)$$

S. S. M. Fernandes et al have prepared three heterocyclic dyes such as 5-aryl-thieno[3,2-b] thiophene is shown in Fig. 1(A) structure, 5-arylthiophene is shown in Fig. 1(B) structure and bis-methyl pyrrolyl thiophene is shown in Fig. 1(C) structure and their properties have redox and optical as well as photovoltaic performance in dye-sensitized solar cells.[22] N. N. Ayare et al have prepared donor-π-acceptor (D-π-A) azo and their properties were high thermal stability.[23] E. R. T. Esmail *et al.* have synthesized thiophene containing Perylene-3,4,9,10-tetracarboxylic diimide, the structure is shown in Fig. 1(D) structure. T-PTCDI is useful in optical and fluorescence emission, absorption dye-sensitized solar cells (DSSC), transistors, push-pulls, biological and organic photovoltaics, and their application as bio-system because of their photochemical properties.[24] The 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)triphenylamine polymer has been synthesized and its structure is shown in Fig. 1(E) structure, and their properties such as transfer capabilities, thermal stability, excellent morphology, and stronger charge separation.[25] The novel thiazolyl azo-dyes bearing coumarin–thiophene moiety have been synthesized and these dyes could be transformed to their original state by adding acid. The dyes have good potential for hydroxide sensing in various mediums.[26] The composites poly(Py-co-Th) (Pyrrole (Py) and thiophene (Th) based copolymers)/ZnO were prepared by the addition of ZnO in various ranges, this composite can be used in organic pollutants management and has excellent photocatalytic enactment to methylene blue than copolymer.[27] The thiophene-based ligands can be used for determining the scientific challenges everywhere protein aggregation diseases.[28] In the last few years, the performance of organic solar cells (OSCs) has been improving owing to the optimization of device fabrication, fine-tuning of morphology, and thin-film processing. The Thiophene fused ring-type non-fullerene acceptors attained noteworthy proficiency for highly efficient OSCs, quantum chemical computations are used for suggesting new NIR-sensitive, low-bandgap materials for OSCs, molecular orbital analysis, density state, excitation energy, transition density matrix analysis, reorganizational energies of both holes (λh) and electrons (λe), and charge transfer. The conjugated A−π–D−π–A architecture novel fused-ring NFAs (FUIC-1-FUIC-6) containing thieno[2,3-b]thiophene-based donor core can be projected by substituting the end-capped units of synthesized molecule F10IC.[29] Seven organic molecules D-A′-π-A structures with thiophene unit as π-bridge linked by dissimilar donor groups of coumarin-based derivatives and diketopyrrolopyrrole (DPP) as the auxiliary acceptor (A′), and cyano-acrylic acid as the acceptor (A), has been considered for potential application in dye-sensitized solar cells.[30]

2 Synthetic procedures of thiophene, and thiophene-based azo dyes

Thiophene can be synthesized at the laboratory and commercial scales using the following major processes below. Fig. 2(A) depicted the 1-Domino of tetra-substituted thiophene synthesized from 1,3-enynes and mercaptoacetaldehyde using DABCO (1,4[diazabicyclo-2.2.2]

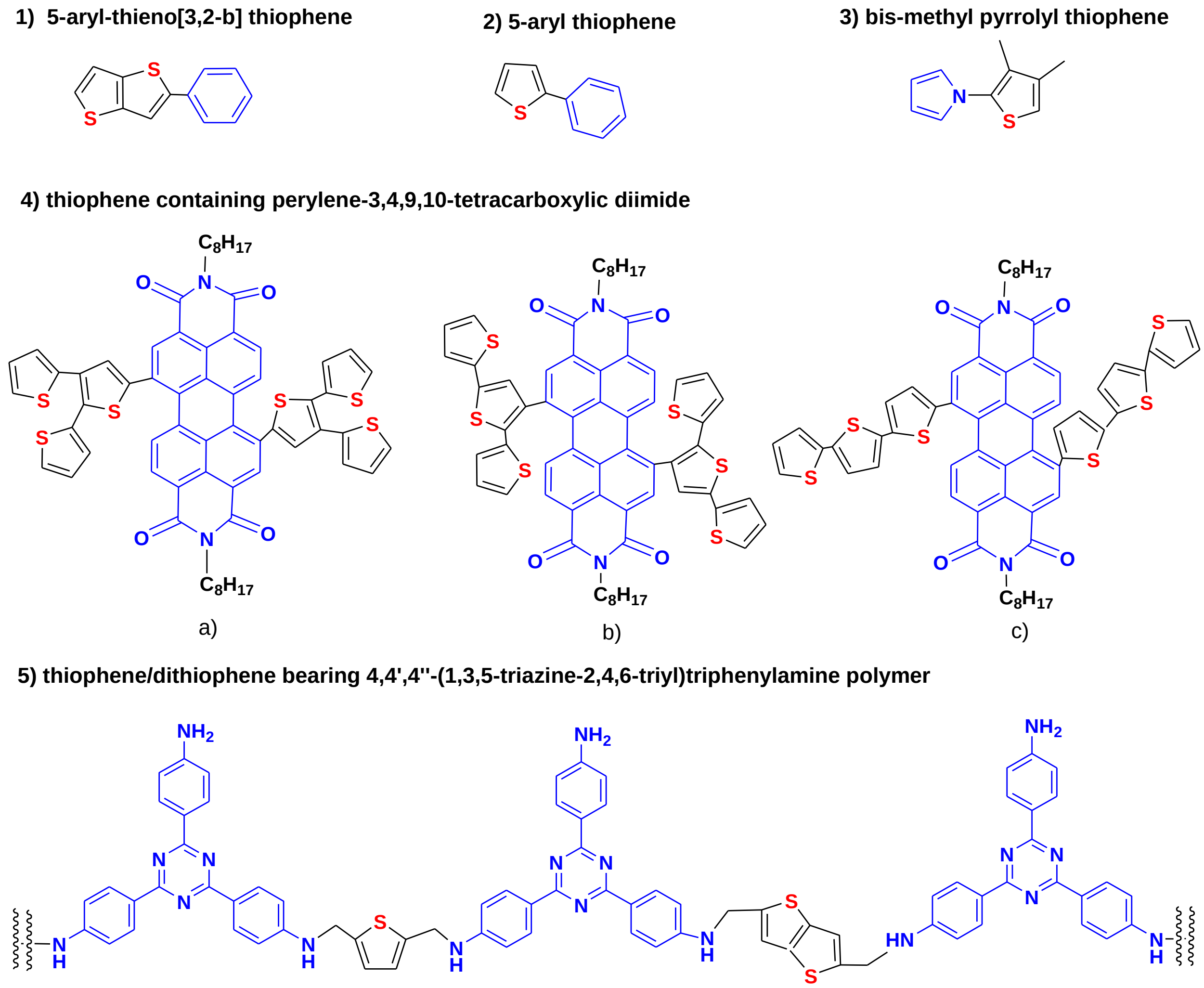
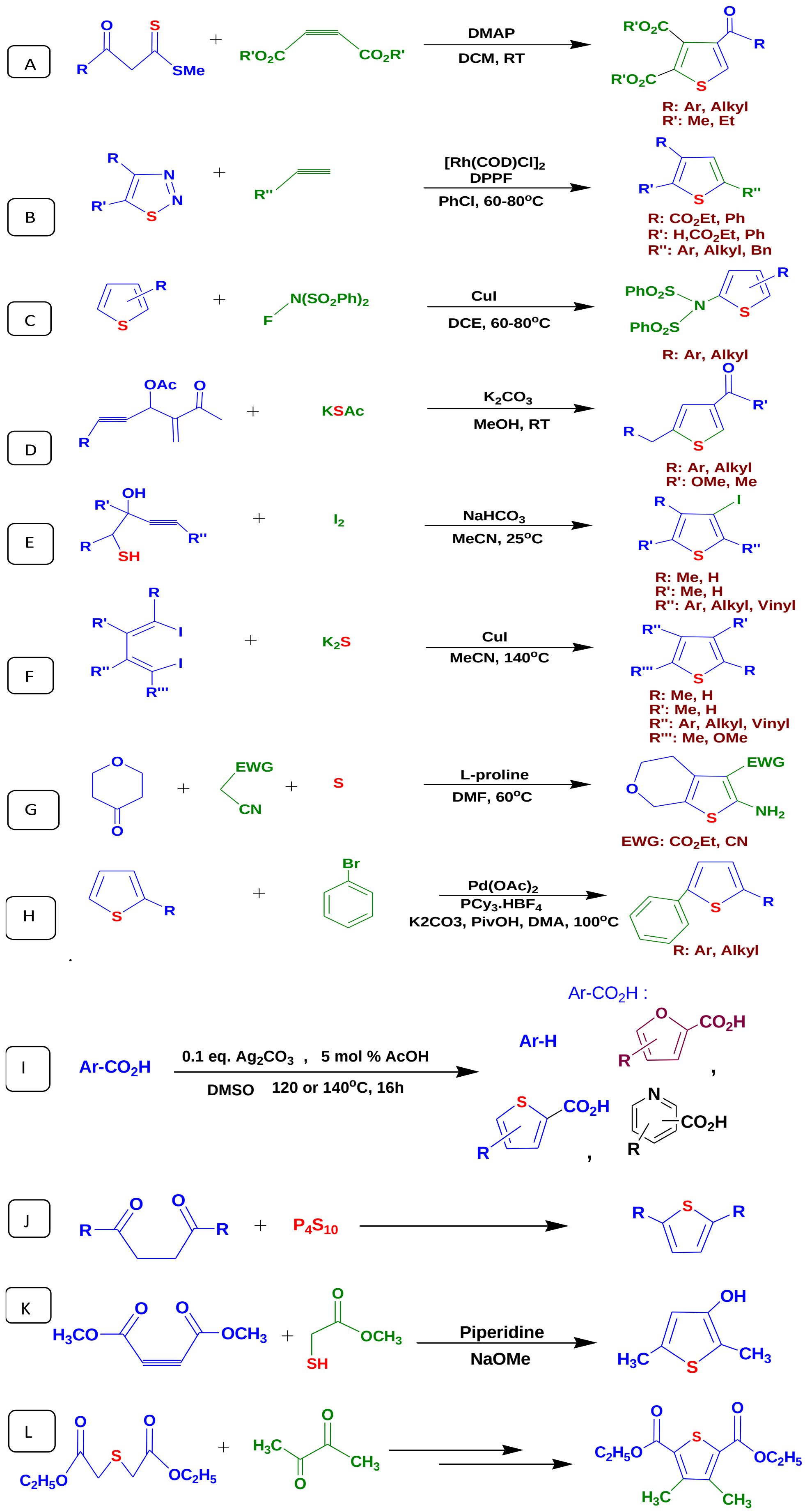


Fig. 1 (1 to 5 structures) Arrangement of thiophene/thieno[3,2-b]thiophene/ trithiophene containing scaffolds possessed various properties.

octane) at room temperature, which offers broad substrate scope and mild reaction conditions. The reaction consists of a Michael addition, 5-exo-dig carboannulation, and oxidation sequence under air.[31] A rhodium-catalyzed transannulation reaction between 1,2,3-thiadiazoles and alkynes enables a highly efficient and regioselective synthesis of highly substituted thiophenes via the intermediacy of a previously unknown Rh this vinyl carbine[8] shown in Fig. 2 (B). A highly efficient amidation reaction of heterocycles with N-fluorobenzenesulfonimide (NFSI) presumably proceeds via C-H bond activation in the presence of cuprous iodide as a catalyst. Various α-amidated heterocycle derivatives have been generated in good to excellent yields[32] as explained in Fig. 2(C). Cross-coupling of aryl bromides with 2-thienyl, 3-thienyl, 2-pyridyl, and 3-pyridyl aluminum reagents in the presence of $Pd(OAc)_2$ and $(o\text{-tolyl})_3P$ provides useful biaryl building blocks in Fig. 2(D). Additionally, the catalytic system was also suited well for the coupling reaction of benzyl halides with pyridyl aluminum reagents to afford a series of pyridylarylmethanes.[33] A mild, metal-free, and base-promoted thio-annulation of Morita-Baylis-Hillman acetates of acetylenic aldehydes with potassium thioacetate to yield substituted thiophenes involves a tandem allylic substitution/deacetylative 5-exo-dig-thiocycloisomerization, shown in Fig. 2(E). The obtained products provide an entry to 4H-thieno[3,2-c]chromene and thieno[3,2-c]dihydroquinoline.[34] A direct iodocyclization of 1-mercapto-3-yn-2-ols derivatives enables the synthesis of 3-iodothiophenes, shown in Fig. 2(F). Various substrates were smoothly converted into the corresponding 3-iodothiophene derivatives in good yields by reaction with molecular iodine in the presence of $NaHCO_3$ at room temperature in MeCN as the solvent.[35] 4-dimethyl aminopyridine (DMAP) promotes an efficient and experimentally rapid protocol for the synthesis of 2,3-dicarboalkoxy-4-aroyl/heteroaryl/alkenoyl thiophenes in high yields via1-2 (C-S) and 3-4 (C-C) bond connections in only 3-5 min in DCM (dichloromethane) at room temperature, shown in Fig. 2(G). This method allows a clean and general synthesis of previously inaccessible and synthetically demanding thiophenes.[36] Fig. 2 (H) shows the copper-catalyzed tandem S-alkenylation of potassium sulfide with 1,4-diiodo-1,3-dienes, which has been used for the synthetic approach to variously substituted thiophenes.[37] An efficient one-pot procedure allows the synthesis of various


A
R'O2C
CO2R'
SMe
DMAP
DCM, RT
R: Ar, Alkyl
R': Me, Et
B
[Rh(COD)Cl]2
DPPF
PhCl, 60-80°C
R: CO2Et, Ph
R': H,CO2Et, Ph
R'': Ar, Alkyl, Bn
C
N(SO2Ph)2
CuI
DCE, 60-80°C
PhO2S
R: Ar, Alkyl
D
OAc
KSAc
K2CO3
MeOH, RT
R: Ar, Alkyl
R': OMe, Me
E
OH
SH
I2
NaHCO3
MeCN, 25°C
R: Me, H
R': Me, H
R'': Ar, Alkyl, Vinyl
F
K2S
CuI
MeCN, 140°C
R: Me, H
R': Me, H
R'': Ar, Alkyl, Vinyl
R''': Me, OMe
G
EWG
CN
L-proline
DMF, 60°C
NH2
EWG: CO2Et, CN
H
Br
Pd(OAc)2
PCy3.HBF4
K2CO3, PivOH, DMA, 100°C
R: Ar, Alkyl
I
Ar-CO2H
0.1 eq. Ag2CO3 , 5 mol % AcOH
DMSO 120 or 140°C, 16h
Ar-H
Ar-CO2H :
CO2H
J
P4S10
K
H3CO
OCH3
Piperidine
NaOMe
H3C
CH3
L
C2H5O
OC2H5

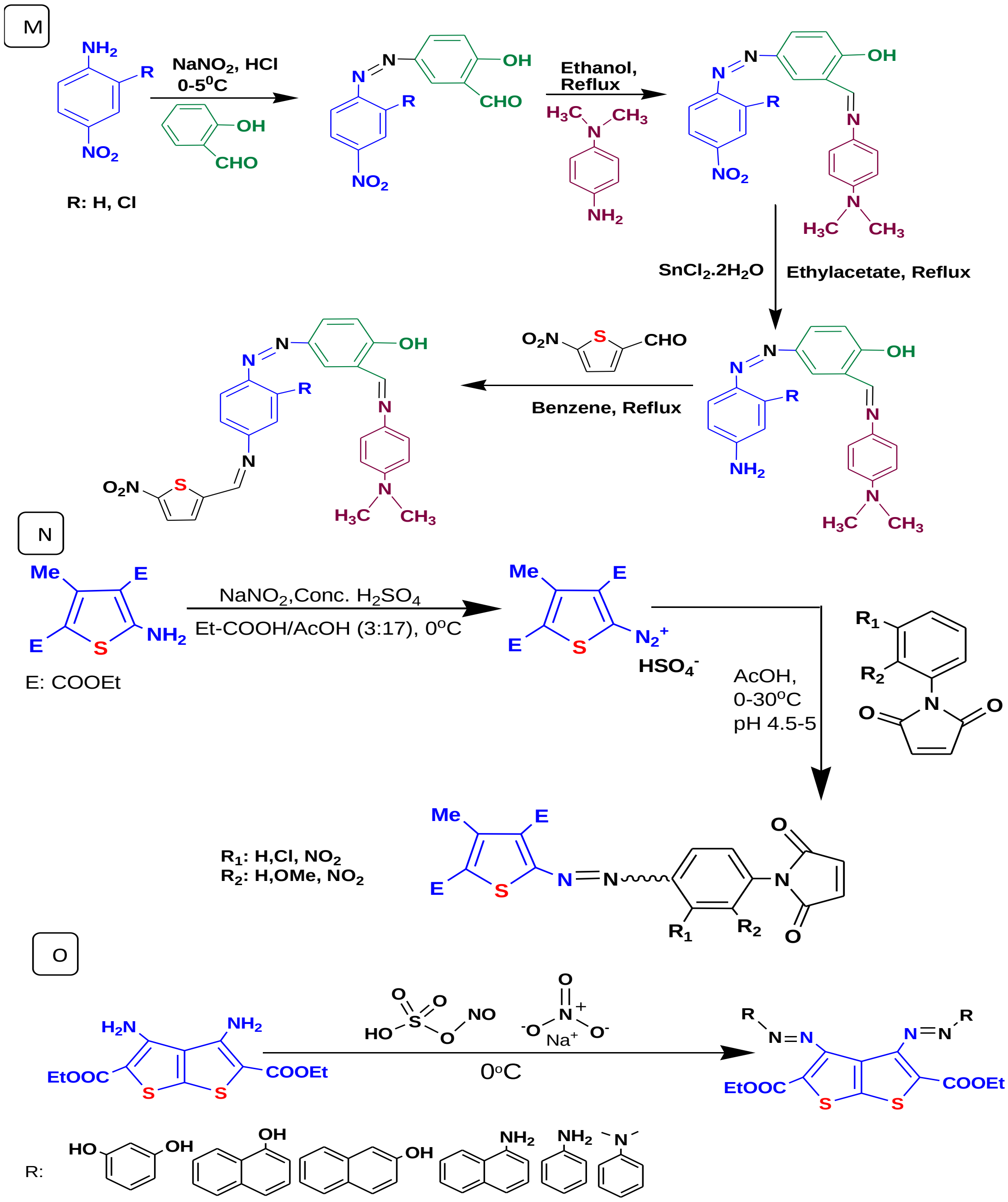


Fig. 2 (A to L) Thiophenederivatives having Therapeutic Scaffolds drugs, (M to O) Thiophene moiety azoderivatives having pharmaceutical Scaffolds drugs M) Fiesselmann Thiophene Synthesis; N) The Hinsberg Synthesis; O) Thieno[2,3-b]thiophene Dye synthesized. A) Domino synthesis of tetrasubstituted thiophenes; B) Rhodium-catalyzed transannulation reaction; C) Amidation reaction of heterocycles with N-fluorobenzenesulfonimide (NFSI); D) Cross-coupling of aryl bromides; E) Morita-Baylis-Hillman acetates; F) Direct iodocyclization; G) Synthesis of 2,3-dicarboalkoxy-4-aroyl/hetero-aroyl/alkanoyl thiophenes from DMAP; H) Copper-catalyzed tandem S-alkenylation; I) functionalized 2-amino thiophene scaffolds catalyzed by L-proline; J) Palladium-catalyzed direct arylation; K) One-pot' procedure with aryl halides under palladium catalysis; L) Paal-Knorr thiophene synthesis. (M to O) Thiophene moiety azoderivatives having pharmaceutical Scaffolds drugs M) Fiesselmann Thiophene Synthesis; N) The Hinsberg Synthesis; O) Thieno[2,3-b]thiophene Dye synthesized.

functionalized 2-amino thiophene scaffolds catalyzed by L-proline in high yields under mild conditions, shown in Fig. 2(I). Low catalyst loading, simple procedure, and high yields are the important attributes of this methodology.[32] Conditions for the palladium-catalyzed direct arylation of a wide range of heterocycles with aryl bromides employ a stoichiometric ratio of both coupling partners, as well as a substoichiometric quantity of pivalic acid, which results in significantly faster reactions, shown in Fig. 2(J). An evaluation of the influence of the nature of the aryl halide has also been carried out.[38] A simple and highly efficient protodecarboxylation of various heteroaromatic carboxylic acids is catalyzed by Ag_2CO_3 and AcOH in DMSO, shown in Fig. 2(K). This methodology also enables a selective monoprotodecarboxylation of several aromatic dicarboxylicacids.[39] Thiophene was regioselectively deprotonated by treatment with Bu_3MgLi in THF at room temperature, shown in Fig. 2(L). The lithium arylmagnesate formed was either trapped with electrophiles or cross-coupled in a 'one-pot' procedure with aryl halides under palladium catalysis.[40] According to Paal- Knorr thiophene synthesis in Fig. 2(M),1, 4-Dicarbony1 compounds are reacted with a source of sulfur to give thiophene while the Microwave-Assisted Paal-Knorr Reaction is a three-step regiocontrolled synthesis for poly substituted as Furans, Pyrroles, and Thiophenes.[41] In the case, the Fiesselmann condensation reaction is shown in Fig. 2(N) of thioglycolic acid with α, β-acetylenic esters, which upon treatment with base results in the formation of 3- hydroxyl- 2- thiophene carboxylic acid.[42] The thiophene has been obtained from two consecutive aldol condensations between a 1, 2-dicarbonyl compound and diethyl thioacetate by the Hinsberg Synthesis method. The immediate product is an ester-acid produced[43] by a Stobbe-type mechanism but the reactions are often worked up via hydrolysis to afford an isolated di-acid. It can be synthesized on an industrial scale by the high-temperature reaction between n-butane and Sulfur. It can be synthesized by passing a mixture of acetylene and hydrogen sulfide through a tube containing alumina at 400°C. This method is commercially used. It may also be prepared by heating sodium succinate with phosphorous trisulphide. S. S. M. Fernandes et al have prepared three heterocyclics dyes such as 5-aryl-thieno[3,2-b]thiophene synthesized by Vilsmeier-Haack formylation, 5-arylthiophene synthesized by Knoevenagel condensation of aldehydes 2–4 with 2-Cyanoacetic Acid, and bis-methyl pyrrolyl thiophene synthesized by Suzuki-Miyaura cross-coupling methods.[22] E. R. T. Esmail *et al.* have synthesized Perylene-3,4,9,10-tetracarboxylic diimide.[24] W. Du has synthesized 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)triphenylamine as the amine unit, and six different aldehyde units as substrates, their results show that thiophene-2,5-dicarbaldehyde (63.27 mg, 0.45 mmol) and 4,4′,4″-(1,3,5-triazine-2,4,6-triyl)triphenylamine (106 mg, 0.3 mmol) were weighed and placed in a dry 25 mL Schlenk tube. The reaction system used a mixed solution of mesitylene (1.5 mL) 1,4-dioxane (1.5 mL), and 6 M acetic acid (0.5 mL) as the solvent then the system was isolated. The device was then sonicated for 30 min to evenly disperse the mixture. Finally, after placing the Schlenk tube in liquid nitrogen to freeze the liquid in the tube, it was subjected to three freeze-thaw cycles to remove the gas. To ensure an oxygen-free environment in the experimental system, it was sealed under a vacuum and reacted at 120°C for 72 h. At the end of the reaction, the device was cooled to normal temperature, and treated by suction filtration, and the solid material was washed repeatedly with anhydrous $CHCl_3$, anhydrous methanol, and anhydrous acetone several times. The obtained solid substance was subjected to Soxhlet extraction with anhydrous THF for 24 h. Finally, the solid material was obtained by filtration and dried in a vacuum drying oven at 80°C. The reaction yielded 135.9 mg (80.29%) of solid with a dark yellow color.[25] The precursors azo compounds were synthesized such as (R]R0]H) by diazotation of 2-amino-4-chloro-5-formylthiazole with nitrosylsulfuric acid, R ¼ $NHCOCH_3$ by copulation on respectively N-phenyldiethanolamine, and R0 ¼ OCH_3 by N-{3-[bis (2-hydroxyethyl)amino]-4-methoxyphenyl}acetamide.[44]

2.1 Synthesis of Novel Azo Dyes Containing the Thiophene Moiety

Disperse dyes are synthesized by diazotization of 2-aminothiophene derivative and coupling with various N-arylmaleimides, and their results give yellowish brown to reddish violet shades on dyeing with very good depth, levelness, and brightness on fabric [63]. Optical characterization and effects of iodine vapor & gaseous HCl adsorption have been investigated for novel organic dye based on thieno[2,3-b]thiophene, they have manifested smaller band gap and more adsorption, and maximum near to solar maximum wavelength, as shown in Fig. 2(O).[70]

3. Applications of Thiophene-based Azo Dyes

A thiophene-based azo dyes class of azo dyes has produced significant interest since its discovery 62 years ago. The applications of thiophene-based azo dyes are dependent on chemical and physical properties. Several azo dyes were achieved by diazo coupling of 4-antipyrinyl diazonium chloride with a variety of coupling components having thiophene moieties. These dyes have good fastness properties for washing, perspiration, rubbing, and sublimation with little variation in moderate to good light fastness.[45] Acetylacetone and malononitrile were coupled with diazotized arylamines to give aryl azo acetylacetone and aryl azo malononitriles; when refluxed with 3-amino-4,6-dimethyl-2-thieno[2,3-b]pyridine carbohydrazide in the presence of glacial acetic acid yielded the corresponding 2-[[4-(aryl azo)-3,5-disubstituted-pyrazol-1-yl]carbonyl]3-amino-4,6-dimethylthieno[2,3,-b]pyridinedyes.[46] The 3-amino4,6disubstitutedthieno[2,3-b]pyridines were diazotized and coupled with 3-aminocrotononitrile to give the 3-(2-hydrozone-3-ketimino-butyronitrile)-4,6-disubstituted-thieno[2,3-b]-pyridines which can react with 85% excess hydrazine hydrate to afford the corresponding 3-(5-amino-3-methyl-pyrazol-4-yl)-azo-4,6-disubstituted-thieno [2,3-b]pyridines.[47,48] These dyes were applied to polyester fibers and showed good fastness properties on polyester fibers.[49] A series of thienyl azo pyrazole dyes[47] were synthesized from the coupling reactions of diazotized poly-substituted 2-aminothiophenes with the corresponding coupling components 5-pyrazolone derivatives. Their solvatochromic properties in different solvents were also investigated.[50] Functionalized thiophene dyes[51,52] were prepared by the reaction of thiocarbamoyl derivatives[37] with a variety of α-halogenated reagents. All of the dyes exhibited very good fastnesses to washing and perspiration, depending on the amount of dye fixed. The light fastnesses of the dyed polyester ranged from a very good yellow-blue axis.[45,53]

Recently, a set of 4-aryl/hetarylazo-3-hydroxy-2-substituted-thiophene disperses dyes.[34,54] were synthesized by hetero-cyclization of ethyl 2-arylhydrazono-2-phenylthiocar bamoyl acetates with several halo-carbonyl reagents, e.g., chloroacetone, phenacyl chloride, and ethyl chloroacetate in the presence of sodium ethoxide. All of them were investigated for their dyeing characteristics on polyester fabric. The dyed fabrics exhibit very good washing and perspiration fastness properties, with little variations in the moderate to good rubbing fastness. The light fastness is moderate although the incorporation of a nitro group in the diazonium components results in an improvement in light fastness to good.[55] Navy disazo dyes containing thienyl middle components have also been marketed and structures, for example (X = Cl, R_1 = CN, R_2 = Et), 82,83,109,110 as well as improved methods, have continued to be the subject of patents. The synthesis of disazo disperse dyes, whereby 2-amino-4,5,6,7-tetrahydro benzo[b]thiophenes are utilized as the first component with phenyl or naphthyl[56] middle components, has been described. Red-brown to blue shades were obtained on polyester, however, light fastness was found to be generally only low. A series of yellow to greenish-blue aziridinyl azo dyes[57] and their azo precursors containing a thienyl coupling moiety[58] and; it has been prepared from 2-amino-4-phenyl thiophene coupling components using conventional diazo coupling reactions and subsequent cyclization in good yield. These dyes are applied to conventional polyester fiber as well as micro-denier polyester by high-temperature exhaust dyeing. The heat transferability of these dyes onto polyester fiber has also been examined, using conventional heat-transfer printing techniques. Fabrics dyed with aziridinyl dyes are more resistant to solvent extraction than those dyed with conventional dyes. Residual liquors showed only a pale colour when fabric dyed with aziridinyl dyes was dissolved and then precipitated, whereas a colored polyester precipitate was obtained. The brilliant red lightfast dyes can be produced by coupling diazotized thiophene amines to diaminopyridines[58-61] and its have excited commercial activity. Structures have also been claimed in which aminothiophenes have been coupled to 2,4,6-triamino-3-cyano-pyridines to yield lightfast red colorants for polyester.[62] Maradiya *et al.* synthesized a series of dispersed polymeric dyes by free-radical polymerization of monomeric dyes that were synthesized by diazotization of 2-aminothiophene derivatives, 2-amino-3-carbethoxy-4,5-dimethylthiophene or 2-amino-3,5-bis-(ethoxycarbonyl)-4-methylthiophene, and coupling with various N arylmaleimides. These dyes were applied as dispersed dyes on nylon and polyester fibers. They were found to give various color shades with good to a very good depth and levelness on the fiber. The variations in the shades of dyed fibers are due to the nature and position of the various substituent present on the maleimide and thiophene ring. The dyeing of the monomeric dyes showed good fastness to light and very good to excellent fastness to washing, perspiration, sublimation, and solvents. The percentage of dye bath exhaustion on nylon fabric has been found to be good and acceptable. Also, the corresponding polymeric dyes showed excellent fastness properties. Thus, the improvement of the fastness properties with increasing the molecular size of the dye molecule by polymerization reaction leads to the brilliancy of shade and excellent fastness properties.[63,64] S. Benkhaya *et al.* synthesized azo dyes and these dyes were shown some technical activities such as reactivity, isomerism, and tautomerism. Bases of linkage of azo dyes are classified as mono-azo, dis-azo, tris-azo, poly-azo, and azoic. According to the color index, azo dyes are provided ranging between from 11000 to 39999 with compound structures such as monozo range of from 11000–19999, disazo range of from 20000–29999, Trisazo range of from 30000–34999, Polyazo range of from 35000–36999, and azoic of from 37000–39999. The index has been developed through the society of Dyers and colorists.[65] H. R. Maradiya *et al.* synthesized a monoazo series of dispersed dyes from coupling 2-amino-3-carbethoxy-4,5-dimethylthiophene using a mixture of N-arylmaleimides. They are used in 2% depth on polyester fabrics and provided light yellow to brown color hues with fair fastness. It was very excellent for rubbing, perspiration, and sublimation.[66] N. Nitesh and Ayare *et al.* have prepared coumarin-based donors (D)-π-azo-acceptor (A) colorants with −COOH and -SO_3H anchoring its application used for dye-sensitized solar cells. NAA 236 colorant shows a short-circuit current density, J_{sc} of ~10.28 mA cm^{-2}, with an open-circuit voltage, V_{oc} of ~0.62 V.[67] E. Kh. Shokr *et al.* prepared the ethanol solution (3 ppm) of some diethyl 3,4-diaminothieno[2,3-b]thiophene-2,5-dicarboxylate (TT amino ester) derivatives, it has revealed that the azo dye derivative.[68] M. M. Rahman *et al.* synthesized 2 novels of 8-hydroxyquinoline-based azo which are made up of two rings, a phenol ring fused with a pyridine ring, and it has been coupled with diazonium salt obtained from 2-amino-6-nitrotoluene (Dye-I) and with the diazonium salt obtained from 4-chloro-aniline (Dye-II)) dyes compounds from artificial strategy and its application were applied for polyester fabric. Color dyes have been analyzed for color fastness to washing, light, rubbing, and perspiration. 8-hydroxyquinoline-based azo has good properties, therefore its demand in PTET fabric textile industries. S. S. M. Fernandes et al have prepared three heterocyclic dyes 5-aryl-thieno[3,2-b]thiophene, 5-arylthiophene, and bis-methyl pyrrolyl thiophene and their higher molar extinction coefficient, long π-conjugation of the heterocyclic system, higher oxidation potential and strong electron-donating capacity of the ethoxyl group.[22,69] E. R. T. Esmail *et al.* have synthesized novel 4-arylazo-3-hydroxythiophene analogs containing sulphapyridine and sulphathiazole dyestuffs. It was applied in dyeing polyester fabrics an application and gave antibacterial efficacy.[24] 2-aryl/hetaryl azo-thiophenes have been used as a dye because of dyeing and fastness properties as shown in Fig. 3(A).[56] Synthesis of 4-aryl azo-2-(Npyrazolylcarboxamido)thiophene disperse dyes for dyeing of polyester and their antibacterial evaluation is shown in Fig.

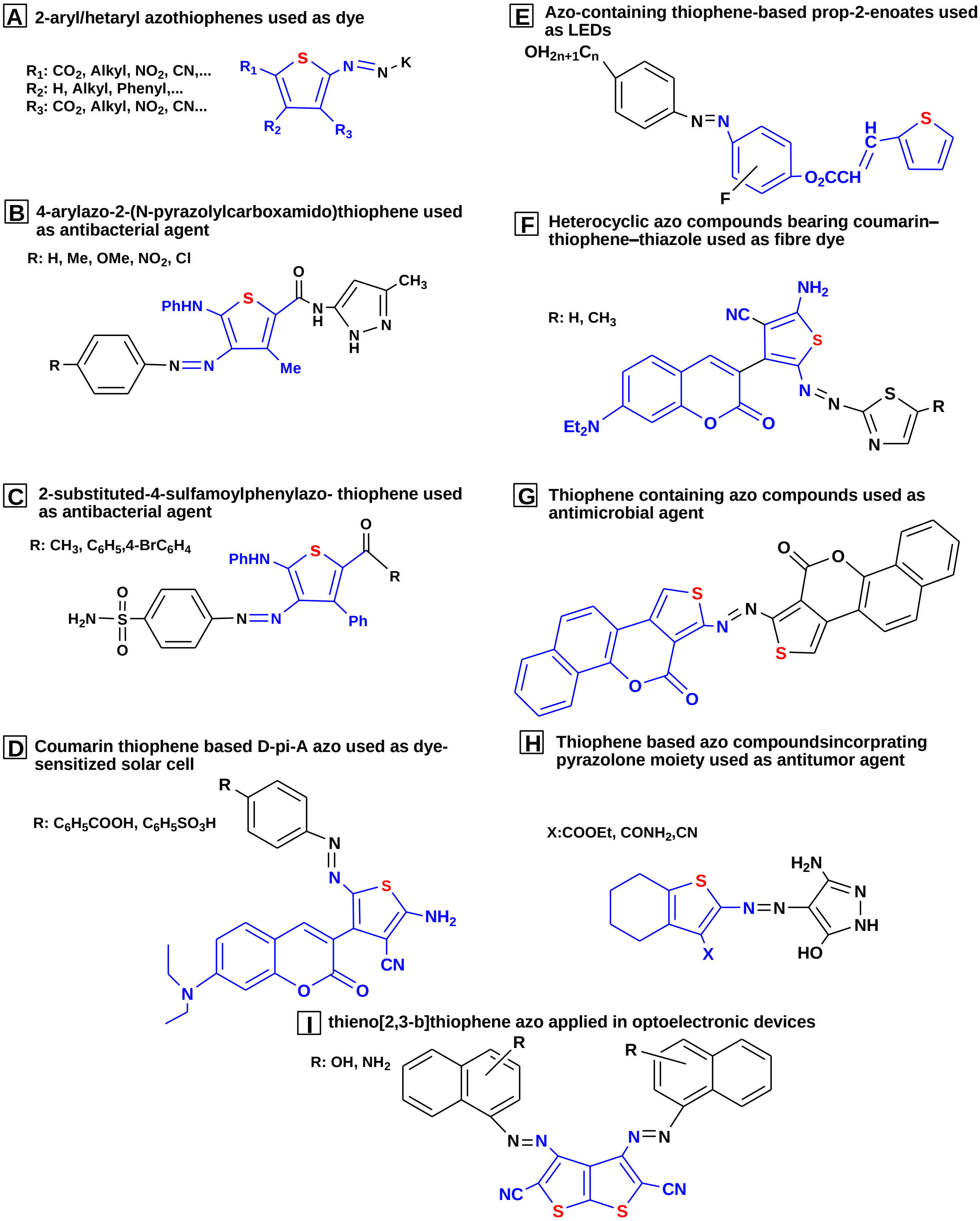


Fig. 3 Thiophene-based azo dyes and their applications in dyes chemistry (A to I structures).

3(B).[71] Synthesis of some new 2-substituted-4-sulfamoylphenylazo-thiophene and/or thiazole derivatives as antibacterial agents is shown in Fig. 3(C).[72] Synthesis and computational study of coumarin thiophene-based D-π-A azo bridge colorants for DSSC and excellent non-linear optical (NLO) response and display a direct relation with photovoltaic performances shown in Fig. 3(D).[73] Prop-2-enoates from 3-(thiophen-2-yl)- and 3-(thiophen-3-yl)-prop-2-enoic acid and appropriately fluorinated and non-fluorinated 4-[(4-alkoxyphenyl)diazenyl]phenols azo contains thiophene-based prop-2-enoates for the photoalignment of a nematic liquid crystal as shown in Fig. 3(E).[74] The syntheses, photophysical properties, and pH-sensitive studies of heterocyclic azo dyes bearing coumarin–thiophene–thiazole is shown in Fig. 3(F).[75] Synthesis and antimicrobial activities of some novel thiophene-containing azo compounds are shown in Fig.

3(G).[76] Thiophene containing pyrazolone moieties was synthesized by diazo coupling of diazonium salt of 3-substituted-2-amino-4,5,6,7-tetrahydrobenzo[*b*]thiophenes with 3-methyl-1*H*-pyrazol-5(4*H*)-one, 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one or 3-amino-1*H*-pyrazol-5(4*H*)-one. The dye is used in polyester fabric as shown in Fig. 3(H).[8] Some novel azo has been synthesized such as thieno[2,3-b]thiophene-2,5-dicarbonitrile derivatives namely; 3,4-bis(2-hydroxynaphthalen-1-yl)diazenyl)thieno[2,3-b]thiophene-2,5-dicarbonitrile,3,4-bis(4-aminonaphthalen-1-yl)diazenyl)thieno[2,3-b]thiophene-2,5-dicarbonitrile and 3,4-bis(4-(dimethylamino)phenyl) diazenyl)thieno[2,3-b]thiophene-2,5-dicarbonitrile. These dyes are applied to optoelectronic devices as shown in Fig. 3(I).[77]

4. Conclusion

The thiophene and thiophene-based azo dyes are valuable for our society, which accounts for the majority of dye manufacturing volume today. Azo dyes are widely utilized in a wide range of various industrial sectors, including food, pharmaceutical, paper, cosmetics, textile, and leather. They account for around half of all synthetic dyes. Furthermore, the results given in this research reveal that thiophene and thiophene-based azo dyes have the broadest variety of applications because chemical structural modifications are easily generated by the interaction of an azo coupling component comprising an atom active hydrogen bound to a carbon atom.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

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