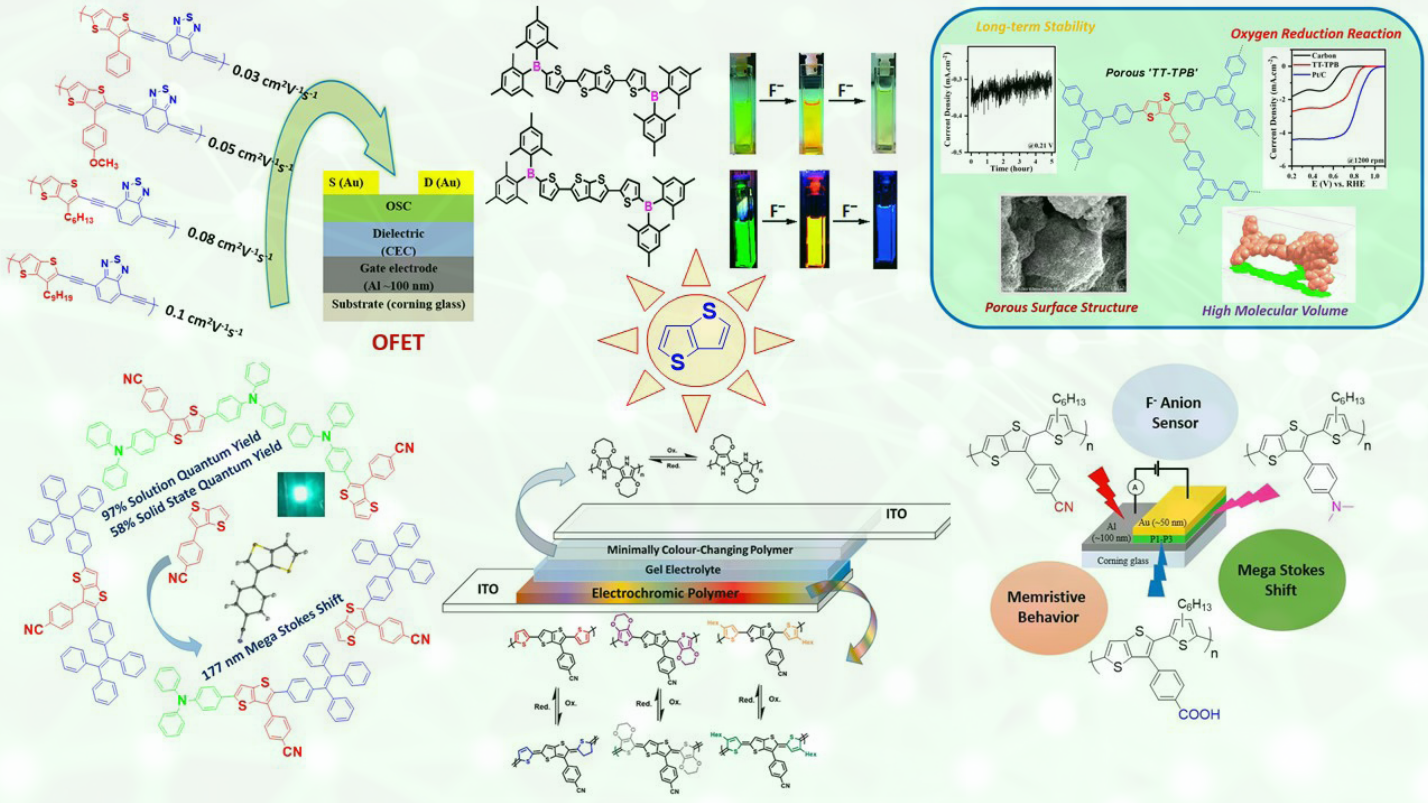
Thienothiophene Based Materials for Organic Electronics



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https://doi.org/10.51167/acm00067

Dr. Recep Isci

Dr. Recep Isci received his PhD in Organic Material Chemistry at Istanbul Technical University (ITU) (2023) under the supervision of Prof. Turan Ozturk on 'synthesis of organic energy materials; investigation of their properties and device applications'. His thesis was supported by government grants (Council of Higher Education YOK 100/2000 and The Scientific and Technological Research Council of Türkiye TUBITAK 2211-A); Smart and Innovative Materials. He took part in Imperial College London, Centre for Processable Electronics as a researcher during his PhD within the 2214-A TUBITAK International Research Fellowship Program.

Prof. Turan Ozturk

Prof. Turan Ozturk received his PhD degree from the University of East Anglia, UK, and then moved to the University of Kent at Canterbury, UK, as a postdoctoral fellow, where he developed a new method for the synthesis of fused 1,4-dithiin and thiophene rings from 1,8-diketones using Lawesson's reagent and P4S10. He took up a position at TUBITAK MRC, Türkiye, then Middle East Technical University, Türkiye, and joined Istanbul Technical University (ITU) as a full professor. He has previously been British Council Research Fellow, NATO Research Fellow and Honorary Lecturer at the University of Kent at Canterbury, and Senior Research Fellow at University of Waterloo, Canada. His research interests concentrate on the development of new organic materials, particularly including thienothiophene and dithienothiophene, having electronic and optical properties.

Thienothiophene (TT) is the simplest fused thiophenes, composed of two annulated thiophene rings. TTs have extended p-conjugation, planar structure, intermolecular S---S interaction, and electron rich, flat, rigid, and good electron delocalized skeleton. These properties make them very suitable and desirable main building blocks for organic electronics.[1-3] They have four structural isomers, thieno[3,2-*b*]thiophene (1), thieno[3,4-*b*]thiophene (2), thieno[2,3-*b*]thiophene (3) and thieno[3,4-*c*]thiophene (4), among which the most widely used form is thieno[3,2-*b*]thiophene (1), providing continuous conjugation through two fused thiophenes for small molecules and polymers (Figure 1).[4-6]

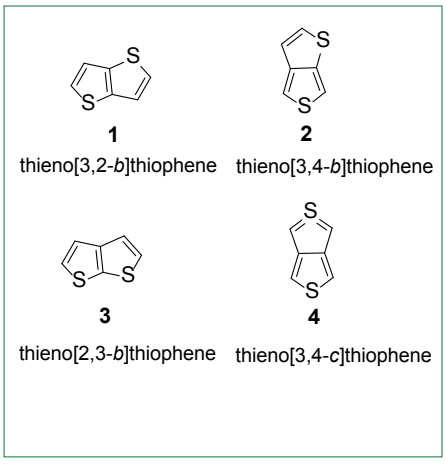
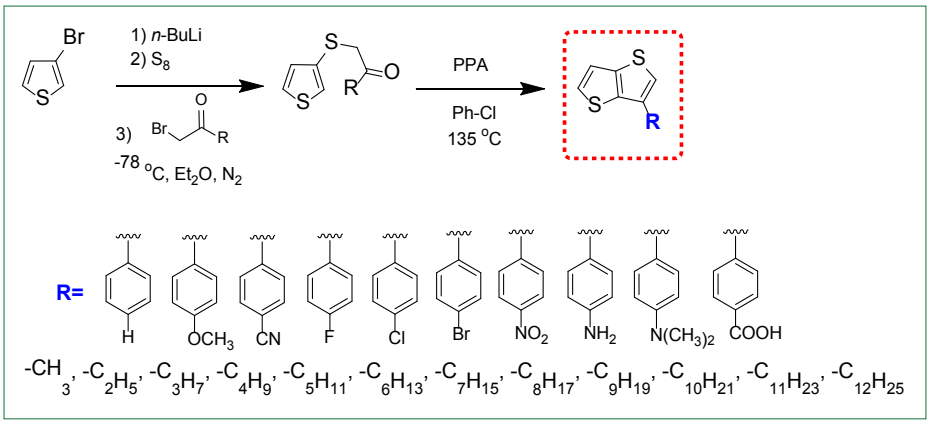


Figure 1. Structural thienothiophene isomers (1-4).

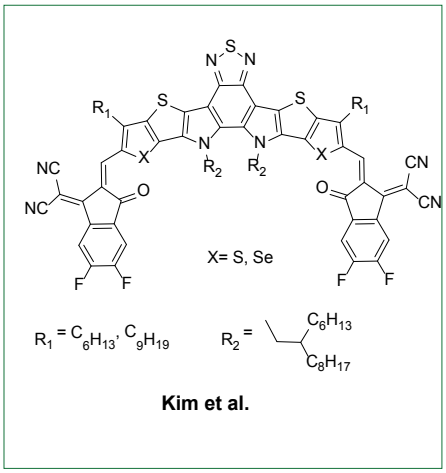
TTs have been attracted a great interest in material chemistry as both polymeric and small molecules for organic electronics such as organic light emitting diodes (OLED), organic field effect transistors (OFET), organic solar cells (OSC), capacitors and sensors.[7-11] Thanks to the versatile properties of TTs, various research groups have focused on TT chemistry, particularly for the development of energy and energy-based smart materials. Our research group is one of the leading one on the development of new synthetic methodologies for the synthesis of substituted TTs. Investigation of the properties, such as electronic and optoelectronic, are also in our expertise. A simple and easy-accessible synthetic strategy developed by

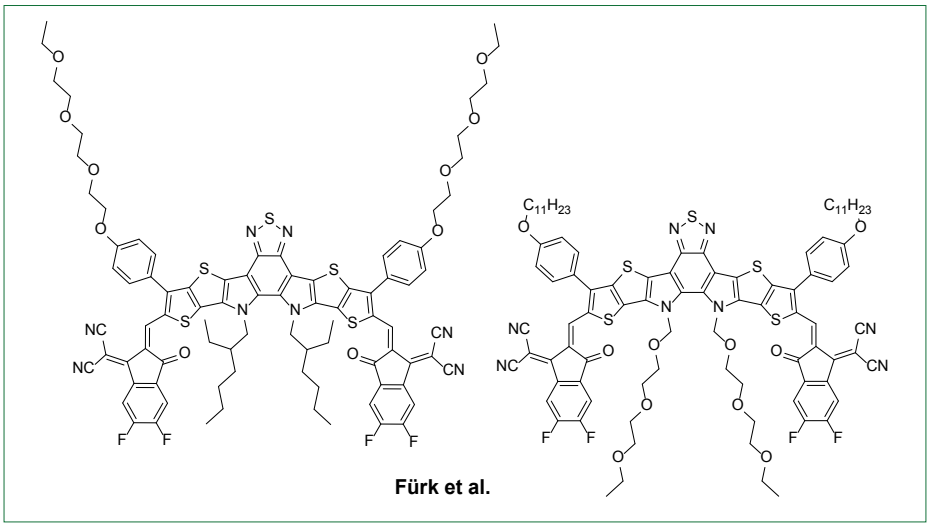


Scheme 1. Functionalized TTs synthesized by Ozturk method in two steps.

Ozturk group has shortened the literature cumbersome four step synthetic method to two steps in high yields, which particularly led to the introduction of various aryl and alkyl groups to the 3-position of thieno[3,2-*b*] thiophene (**Scheme 1**).[12-16]

The Ozturk method has now been used by some research groups and notified as a convenient synthetic method; "…synthesis was done via an alternative synthetic route, which simplifies the variation of the side chains in the outer thiophene site via a universal thienothiophene building block that can be prepared with good yields from inexpensive starting materials" (**Figure 2**).[17-19]





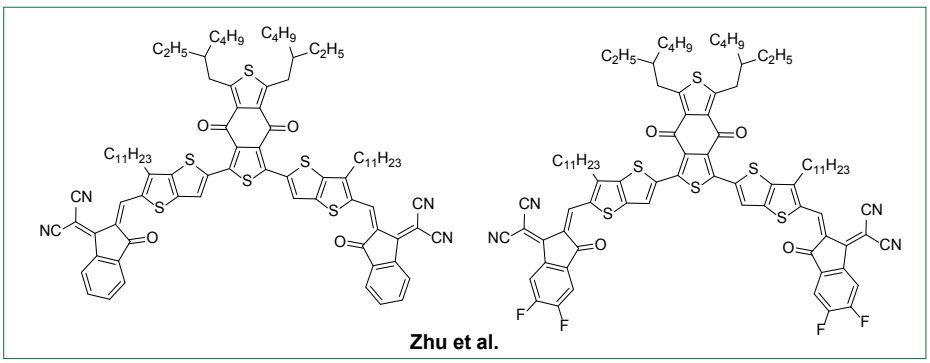


Figure 2. Structures of TT based materials synthesized using Ozturk method.

Functionalized TTs have been very productive building blocks for the preparation of various organic materials. In this overview, some recent TT units having various functional groups, developed by Ozturk Research group, and their use in organic electronic and optoelectronic applications are summarized.

Fluorescence and Organic Light Emitting Diode (OLED) Applications

In 2020, Isci et al. disclosed TT, DTT (dithienothiophene) and TPE (tetraphenylethylene) based small fluorophores (**TT-TPE2**, **DTT-TPE2** and **TT-TPE3**) having AIE (aggregation-induced emission) behaviors (Figure 3).[20] They showed interesting optic and electronic properties depending on the positions of the TPE units at the peripheries of TTs and DTT. **TPE2-TT** produced an excellent device performance with a maximum luminance of 11620 cd.m^{-2} and a maximum current efficiency of 6.17 cd. A^{-1}. The highest solid-state quantum yield was obtained with **TPE3-TT** (28%), the second one was **TPE2-TT** (21%) and the lowest was found to be **TPE2-DTT** (14%). This order indicated that as the planarity was increased a lowest quantum yield was obtained.

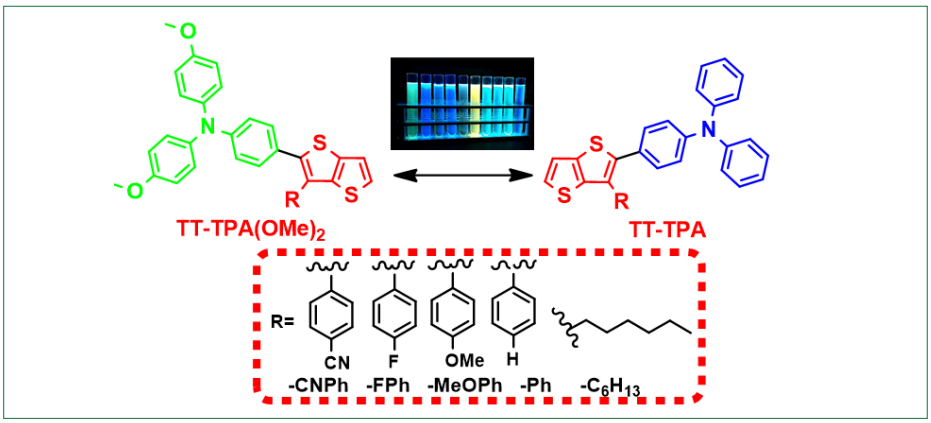


Figure 4. TT and TPA based fluorescent materials having high quantum yields.

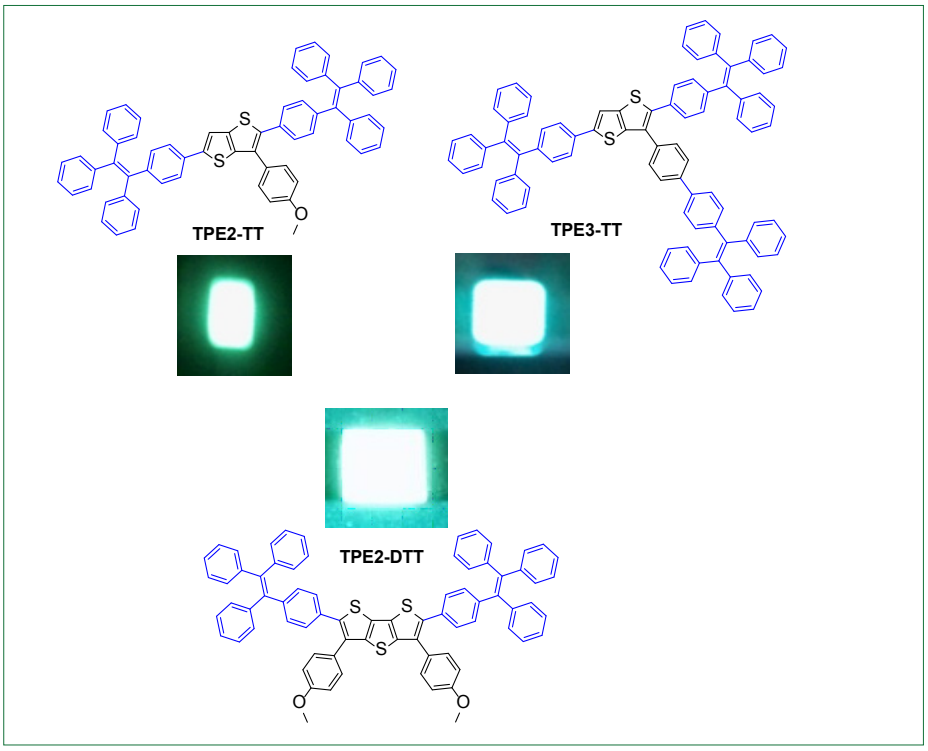


Figure 3. TT, DTT and TPE based OLED materials.

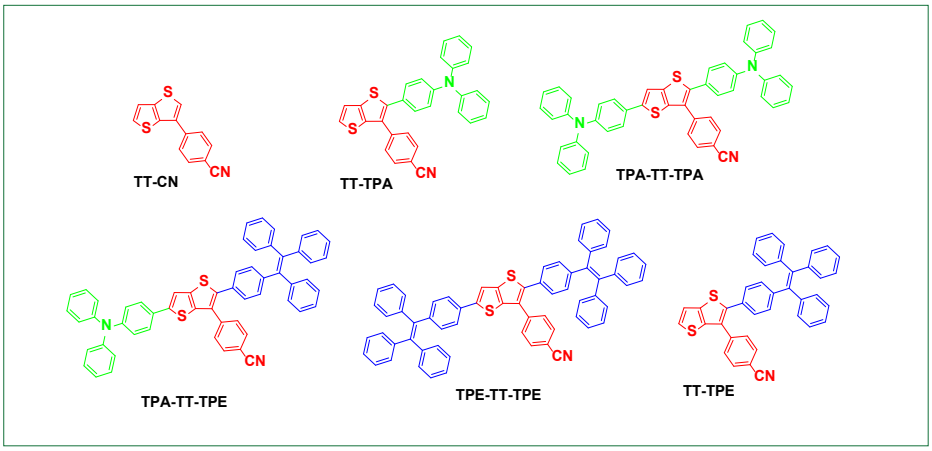


Figure 5. TT, TPA and TPE based OLED materials.

As a continuation of our study toward new effective fluorophores with high quantum yields, a series of TT fluorophores possessing various electron-donating and -accepting functional groups (4-CNPh, 4-FPh, 4-MeOPh, Ph, and C_6H_{13}) and triphenylamine (TPA)/ 4,4′-dimethoxytriphenylamine ($TPA(OMe)_2$) moieties were designed and synthesized by Isci et al. in 2021 (Figure 4).[21] Their solid-state quantum yields (QY) varied from 20 to 69%, while the solution state varied from 31 to 97%. Moreover, the materials showed mega Stokes shifts up to 179 nm, wide range of fluorescence color from greenish to dark blue, the optical band gaps ranging from 2.86 to 3.08 eV and fluorescence lifetime from 2.05 to 4.70 ns, which are higher values compared to many TTs and triarylamine fluorophores available in the literature.

Five novel fluorescent materials, TT-TPA, TT-TPE, TPA-TT-TPA, TPE-TT-TPE and TPA-TT-TPE, containing a strong electron donating triphenylamine (TPA) and an AIE luminogen tetraphenylethylene (TPE), linked through a thienothiophene, 4-thieno[3,2-b] thiophen-3-ylbenzonitrile (TT-CN), possessing a strong electron withdrawing nitrile moiety, were systematically designed, synthesized and their optic and electrochemical properties were compared (Figure 5).[22]

Their solid-state quantum yields were recorded to be between 9 to 58% and solution quantum yields were reached up to 97%. As the compounds had suitable solid-state quantum yields, their OLEDs were fabricated, which had performances with a maximum luminance of around 2800 cd.m^{-2} and a maximum current efficiency of 4.70

cd A^{-1}. They displayed emission colors from blue to green and yellowish green (Figure 6).[22]

As a continuation of TT and TPA combinations for OLED applications, donor-p-acceptor (D-p-A) type novel two pull-push materials, M1 and M2, having TPA as a donor and dimesitylboron as an acceptor, linked through TT p-conjugated spacer bearing different functional substituents, such as -PhCN, and -Ph, were synthesized and fabricated via solution process for OLED applications (Scheme 2).[23]

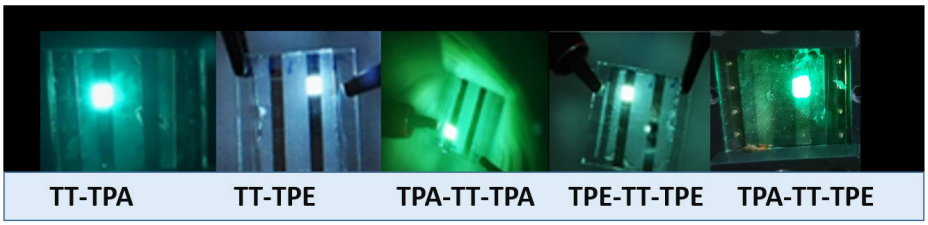
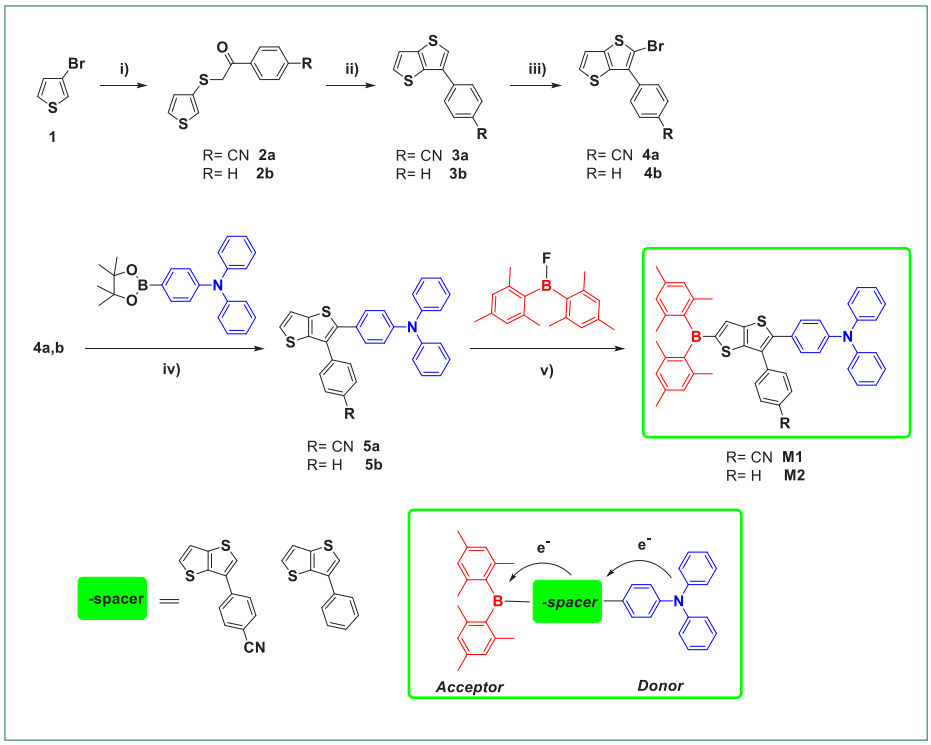


Figure 6. Fabricated device photos of compounds during light emission.



Scheme 2. Syntheses of M1 and M2. Reagents/conditions: i) n-BuLi, S_8, alfa-bromoketones, Et_2O, -78 °C to rt.; ii) PPA, chlorobenzene, reflux; iii) NBS, DMF, -10 °C; iv) 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-triphenylamine, $Pd(PPh_3)_4$, K_2CO_3, THF, 80 °C; v) t-BuLi, dimesitylboron fluoride, THF, -78 °C to room temperature.

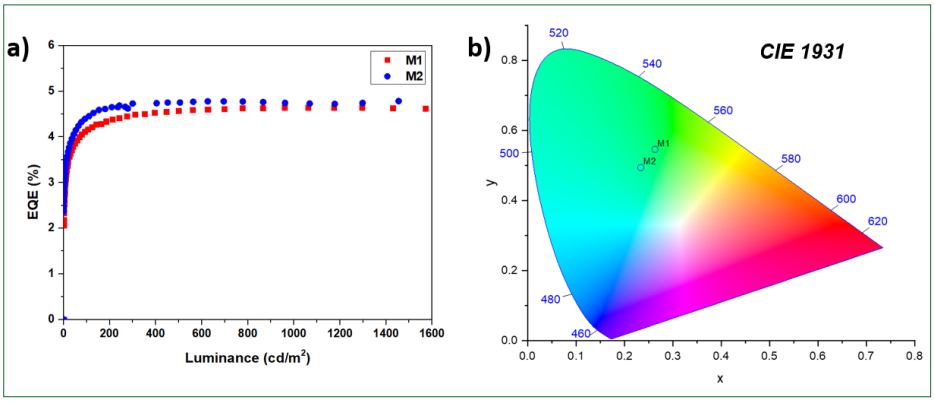


Figure 7. (a) External quantum efficiency-Voltage, (b) CIE color gamut diagrams of M1 and M2.

M1 and M2 displayed remarkable properties of perfect solution and solid-state quantum efficiencies reaching 100 and 76% and a mega Stokes shift of 120 nm. Their devices, prepared by solution process, had max current and power efficiencies of 14.1 cd/A and 7.94 lm/W, respectively (Figure 7).[23]

Organic Field Effect Transistor (OFET) and Memory Applications

In 2022, synthesis of four novel donor-acceptor conjugated copolymers (P1-P4) comprising electron rich thieno[3,2-b]thiophene units to act as donor and 4,7-diethynylbenzo[2,1,3]thiadiazole as an acceptor were reported (Figure 8).[24]

The polymers were fabricated as OFET devices using low voltage energy. They displayed p-channel field-effect behavior and successfully operated below -3 V in high yield. P1-P4 showed maximum operation performances with average saturated hole mobility of 0.1 cm^2/Vs, on/off ratio of 3.5×10^3 and subthreshold swing < 200 mV/dec (Figure 9).[24]

Another functional TT based organic resistive memory devices were operated using π-extended conjugated three novel polymers (P1-P3) possessing cyano (CN), carboxylic acid (COOH) and dimethylamine ($N(CH_3)_2$) substituted TT and 3-hexylthiophene units by Gunturkun et al. in 2022 (Figure 10).[25]

The memory devices of P1-P3 exhibited a high ON/OFF ratio reaching up to 10^6, displaying an excellent conductivity as a suitable fast response data storage polymer. Moreover, all the polymers showed good retention without any degradation in both OFF- and ON-states under a constant stress of -1 V. The TT-based polymers, having varying functional groups, presented in this study, were found to be suitable active materials for high-performance memory devices (Figure 11).[25]

Another TT based OFET study was operated using cyanoethyl cellulose (CEC) as a dielectric layer in BGTC device architect (Figure 12).[26] Novel conjugated donor-p-acceptor-p (D-p-A-p) type polymers, possessing thieno[3,2-b]thiophene (TT) with different aromatic substituents as donors, benzo[2,1,3]thiadiazole (BT) as an acceptor and thiophene as a p-linker were designed and synthesized via palladium-catalyzed Stille coupling reaction. A highest p-type OFET performance with hole mobility up to 0.04 $cm^2V^{-1}s^{-1}$, average Ion/Ioff ratio of 3×10^3 and the smallest subthreshold swing, SS, of 250 $mV.dec^{-1}$ was achieved.

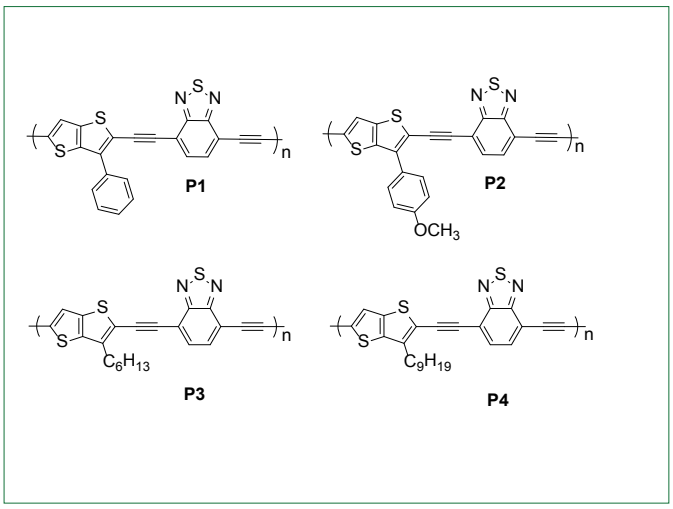


Figure 8. TT and benzothiadiazole based OFET materials

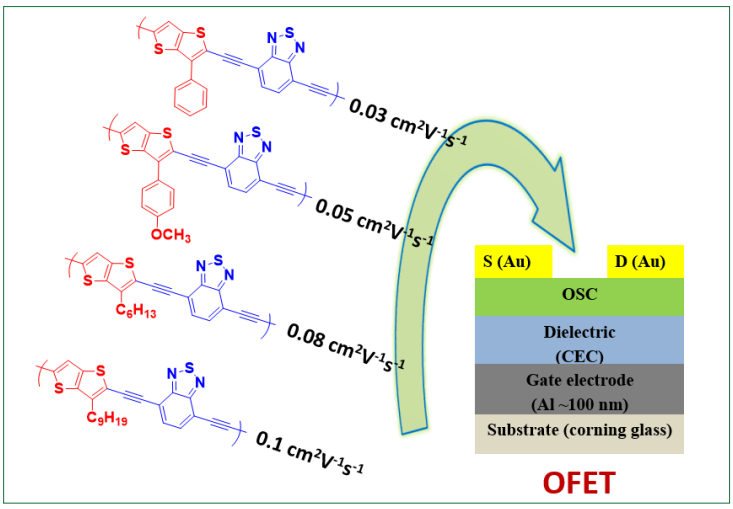


Figure 9. Device architect of P1-P4.

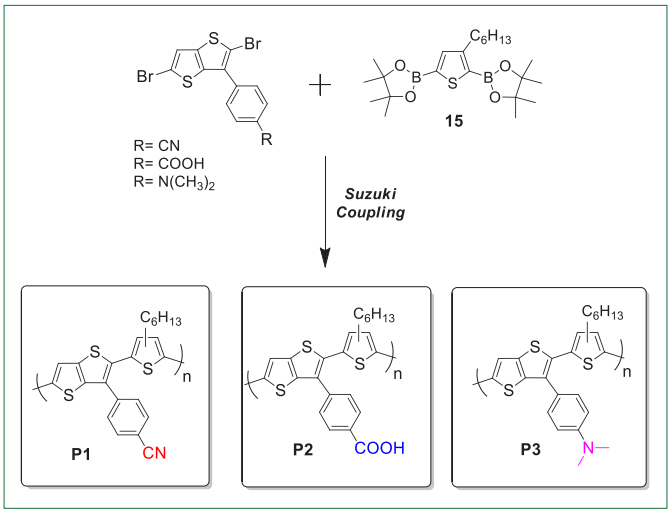


Figure 10. TT and 3-hexyl based copolymers, P1-P3.

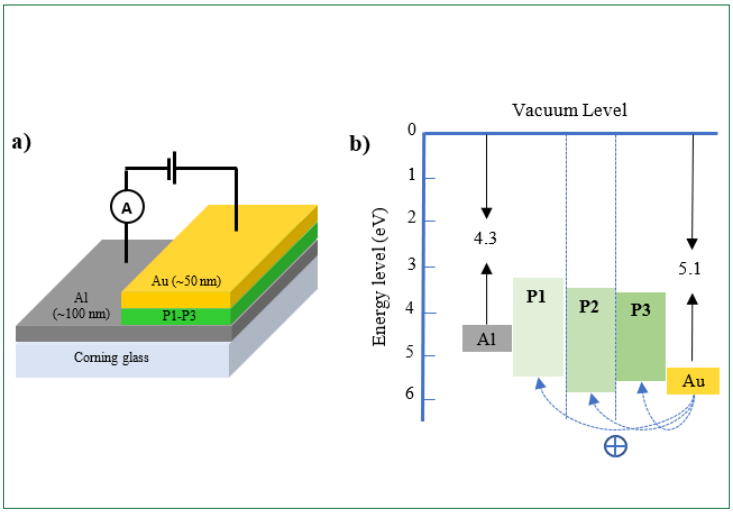


Figure 11. Memory device architect of P1-P3.

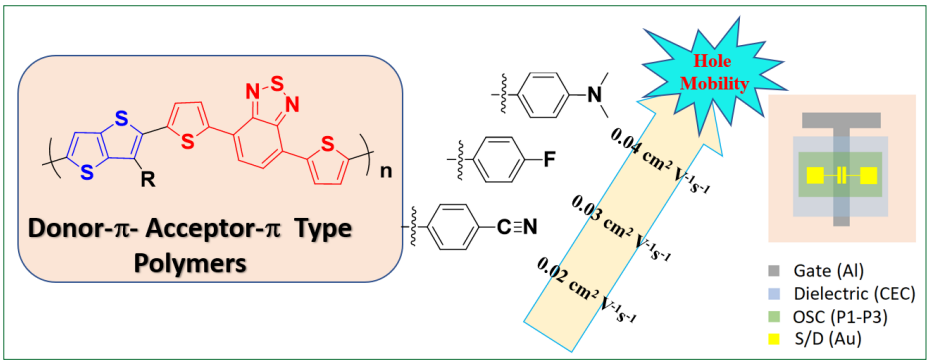


Figure 12. Device architect of D-π-A-π type polymers.

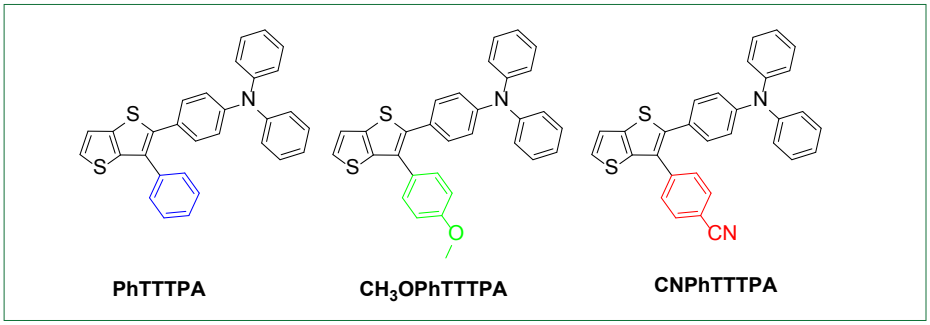


Figure 13. The structure of PhTTTPA, CH_3OPhTTTPA and CNPhTTTPA.

Capacitor and Electrocatalytic Applications

Considering that TTs could be suitable materials for capacitor and electrocatalytic applications, materials possessing both TT and TPA, i.e. **PhTTTPA**, **CH_3OPhTTTPA** and **CNPhTTTPA**, were designed, synthesized and their corresponding polymers (**P[PhTTTPA]**, **P[CH_3OTTTPA]** and **P[CNPhTTTPA]**) were prepared by electrochemical polymerization (**Figure 13**).[27] Then, the influence of the substituted groups Ph, CH_3OPh and CNPh on the capacitive properties of the polymers were investigated. The electropolymers reached to maximum specific capacitance value of 198.2 $F.g^{-1}$ and coating capacitance value of 1232 $F.g^{-1}$ from equivalent circuit model (**Figure 14**).

Separately, a monomer possessing dithienothiophene (DTT) and triphenylamine (TPA) units were subjected to electropolymerization by Topal et al for energy store application (Figure 15).[28] Thus, a microporous hybrid material, having smart charge property, controlled by color change, was

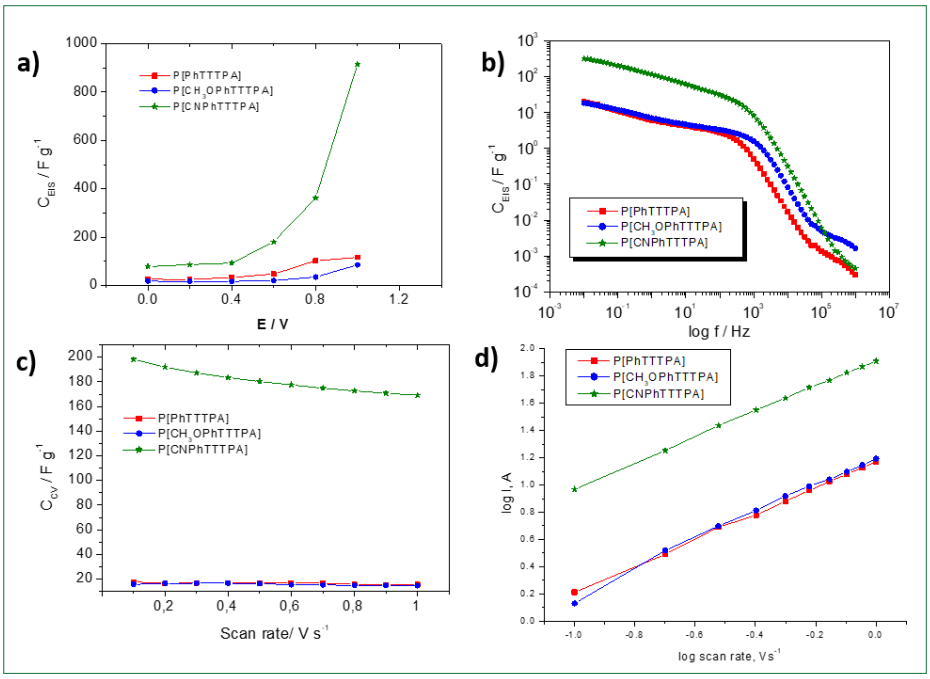


Figure 14. a) Variation of a capacitance values (C_{EIS}) with potentials, b) Variation of C_{EIS} values with frequency. c) Variation of Ccv values with scan rates d) Log current-log scan rate relationship for electropolymers.

reported. It showed a high specific capacity of 54 mA h g^{-1}, a high capacitance of 242 F g-1 at 0.5 A g-1 and a high energy density of 43 W h kg-1 at current density of 10 A g^{-1}. Symmetric energy storage device worked at a high voltage (3 V) and lit a red lamp for several seconds.

Three new π-conjugated TT based monomers having thiophene, 3-hexylthiophene and EDOT at the peripherals were synthesized by Demirtas et al (Figure 16).[29] Their electropolymerization produced the corresponding electroactive polymers, which exhibited electrochromic properties with color developments from red to blue, orange-yellow to pale-blue and purple to pale-grey, respectively. Their electrochromic devices (ECDs) were constructed, which showed a lower contrast in the NIR region (8-21%) and a decent contrast in the visible region (20-34%). They had modest switch times of 1.2-1.7 s for bleaching and 0.9-1.7 s for coloring.

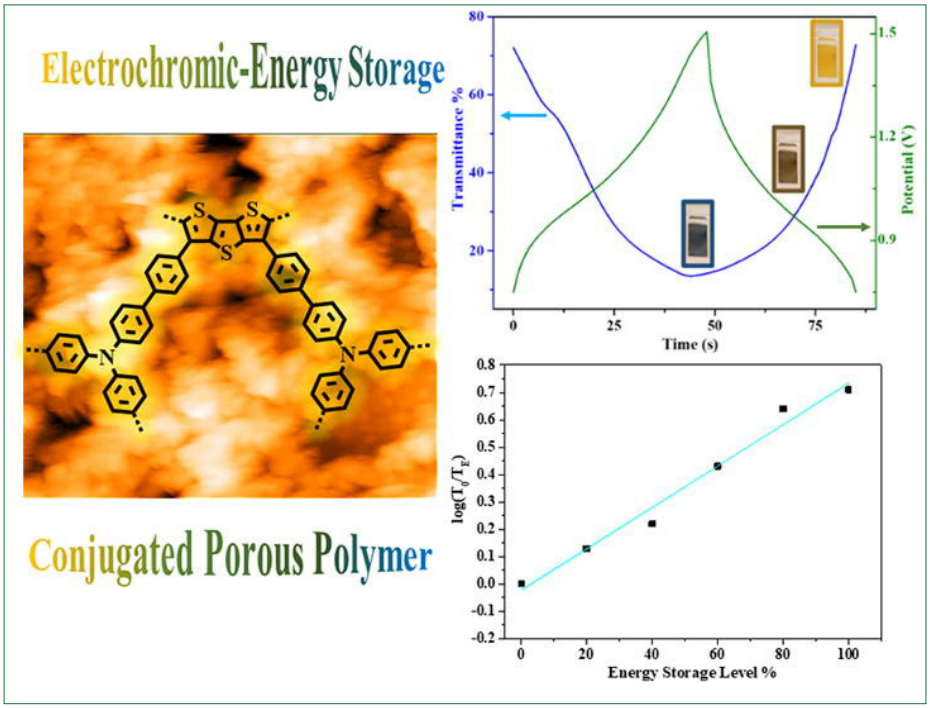


Figure 15. DTT and TPA based porous polymer.

As TT-based porous materials have the potential of acting as a metal free electroctalyst, a new conjugated porous polymer (CPP), TT-TPB, as a metal-free electrocatalyst, was designed and synthesized by Isci et al (Figure 17).[30] It demonstrated activity toward oxygen reduction reaction (ORR) with a comparable electrocatalytic performance of ≈0.89-0.9 V E_{onset} vs RHE with the commercially available Pt/C. The distance between the farthest atoms on the main core and the total volume were calculated to be 19 Å, and 9300 $Å^3$, respectively. The HOMO level was determined to be higher than LUMO level of O_2, proving a perfect porous active side and adsorption of O_2 molecule onto the TT unit. This work could open a new way to construct electrocatalysts with TT and TPB core as active site for efficient catalytic reactions in conversion applications.

Sensor and Functional Applications

As an outstanding example of functionalized TTs, first example of noncovalent functionalization of sidewalls of SWCNT (single wall carbon nanotube) using thienothiophene (TT) derivatives without requiring any binding agent (Figure 18) was released.[31] The synthesized TT derivatives attached directly to SWCNT through noncovalent interactions to produce new TT based SWCNT hybrids, which were clarified by both experimental and theoretical analyses. The minimum distance between the TT and SWCNT reached up to 3.5 Å, identified with strong peaks on radial distribution function (RDF), shorter than Van der Waals interaction.

As a TT based sensor application, first triple-channel fluorescent probe, TTB, excited at the same wavelength (λ_{ex} =360 nm) in the same sensing medium for detection and discrimination of cyanide, hydrazine, and hypochlorite, was disclosed by Suna et al (Figure 19).[32] While a fluorescent white color appeared (λ_{em} =470 nm) with the addition of cyanide ion into the probe solution, upon addition of hydrazine and hypochlorite, green (λ_{em} =503 nm) and orange (λ_{em} =585 nm) fluorescent colors, respectively, were observed. Remarkably, the probe successfully detected cyanide, hydrazine, and hypochlorite in complex water samples. Moreover, detection of cyanide was successfully performed in apricot kernels, as well as hypochlorite in fruits and vegetables.

As chemosensor and fluorescent sensor applications, two novel organoboron compounds, possessing conjugated thieno[3,2-*b*]thiophene and cross-conjugated

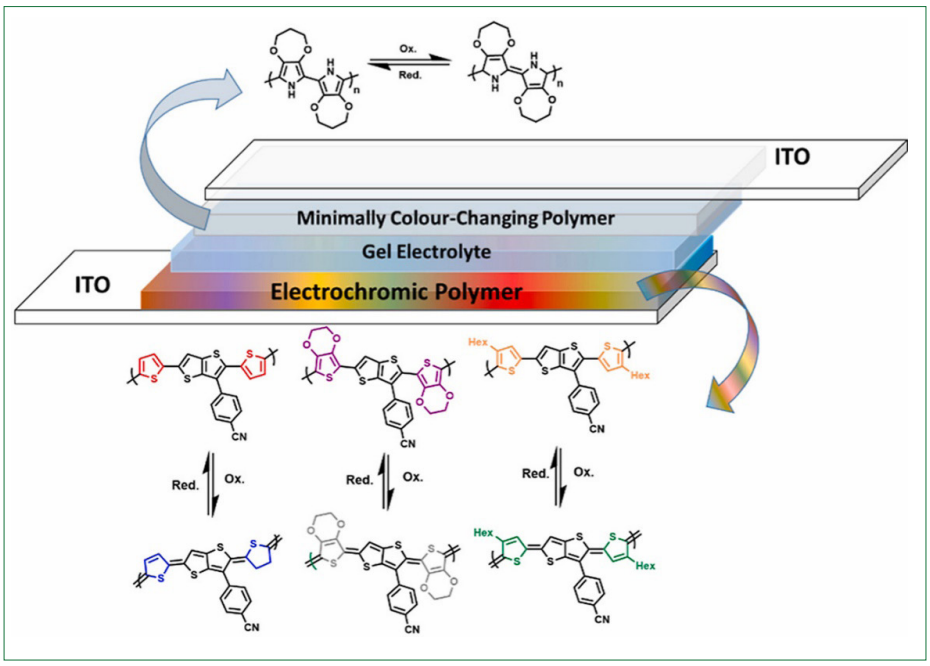


Figure 16. TT based electrochromic electropolymers.

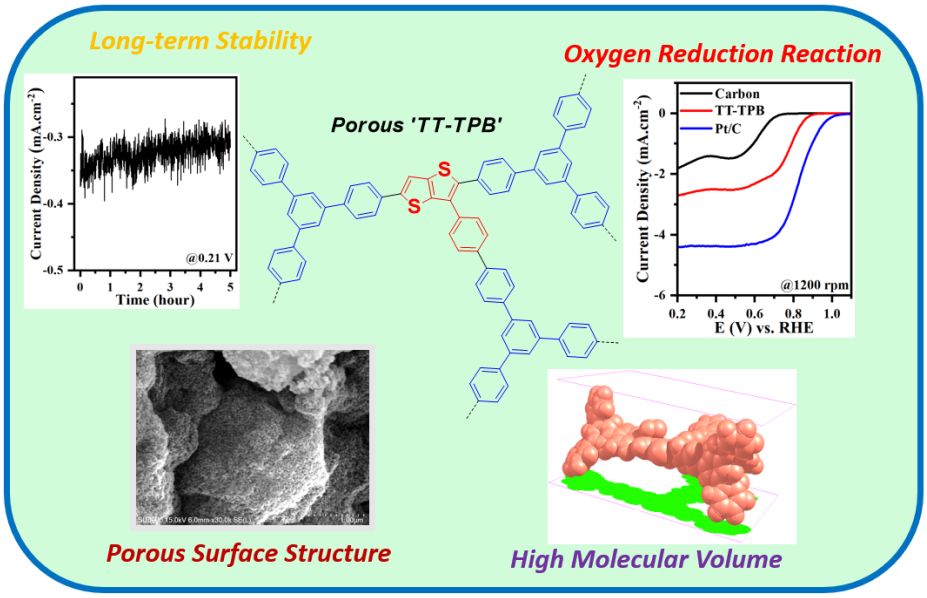


Figure 17. TT based conjugated porous polymer, TT-TPB.

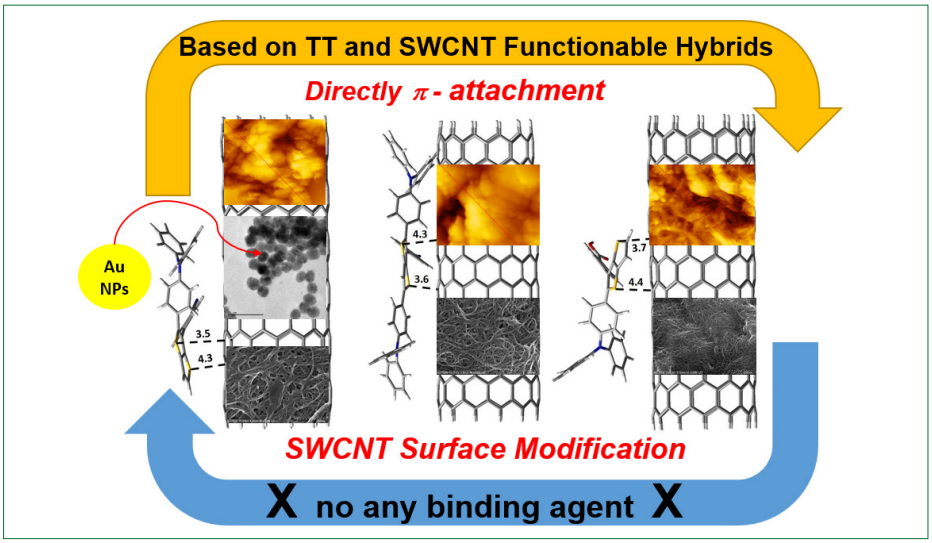


Figure 18. TT and SWCNT based hybrid materials.

thieno[2,3-*b*]thiophene, respectively, as electron donors and bis-triarylboron units as electron acceptors linked through thiophene π-spacers were synthesized and structurally characterized through spectroscopic methods (**Figure 20**).[13] The compounds acted as colorimetric and fluorescent chemosensors with high sensitivity and selectivity towards F^- anion showing turned on chemosensor and turned off fluorescent sensor. The study is expected to advance the ongoing investigations into optoelectronic applications and the design of novel organoboron π-conjugated derivatives with outstanding sensing properties.

CONCLUSION

Within the scope of this overview, importance of TT units for organic electronic and optoelectronic is revealed. Thus, TTs and that they have a great place in material chemistry. Thus, some functionalized TT examples, developed by our group for OLED, OFET and sensor applications are presented. We hope that these case studies will shed light on the next generation of future studies and material science in many ways.

Acknowledgement

We thank Higher Education Council of Türkiye (YOK) and TUBITAK grants to Recep Isci (PhD, 100/2000 YOK, 2214A and 2211A BIDEP/TUBITAK). The authors thank ITU (Istanbul Technical University), TGA-2021-42949 numbered ITU BAP Project and Unsped Global Lojistik, Türkiye, for financial supports.

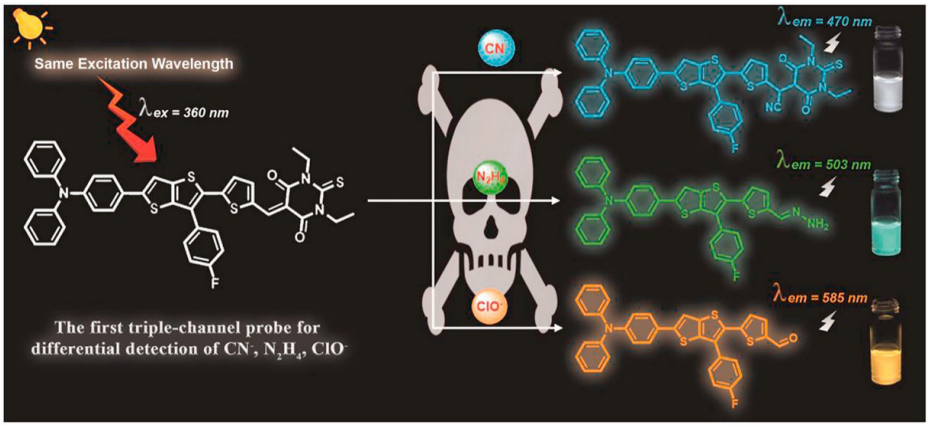


Figure 20. TT and boron based chemosensor and fluorescent sensor.

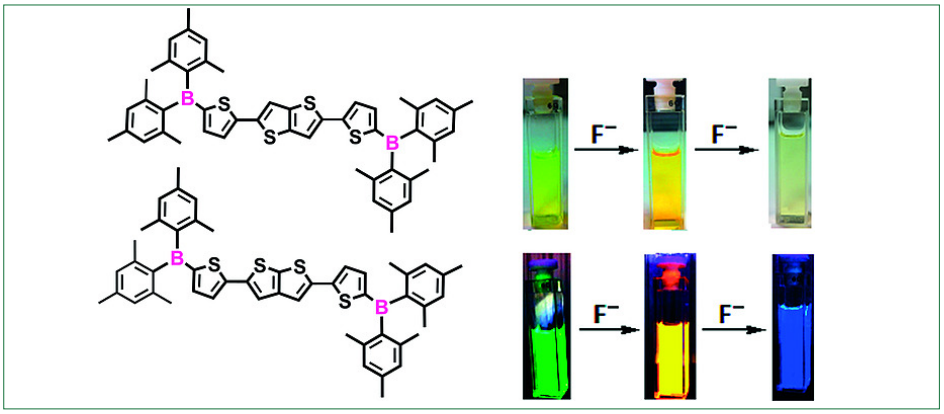


Figure 19. TT based triple-channel fluorescent probe.

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