CHEMISTRY & CHEMICAL TECHNOLOGY

Chem. Chem. Technol., 2025,
Vol. 19, No. 1, pp. 52–60

Chemistry

MODIFICATION BY FLUORINE AS EFFICIENT TOOL FOR THE ENHANCEMENT OF THE PERFORMANCE OF ORGANIC ELECTROACTIVE COMPOUNDS – A REVIEW

***Mariia Stanitska**[1,2], **Mykola Obushak**[2], **Juozas Vidas Gražulevičius**[1,✉]*

https://doi.org/10.23939/chcht19.01.052

Abstract. Functionalization of organic semiconductors with fluorine atoms and fluorine-containing groups can give rise to a wide variety of properties, for example, increase the rate of electron transport, induce harvesting of non-emissive triplet excitons through thermally activated delayed fluorescence (TADF) or room temperature phosphorescence (RTP), improve photoluminescence quantum yield (PLQY) by forming multiple intra- and intermolecular interactions, and increase solution-processabitily of the compounds, therefore, lowering the cost of device fabrication. Diverse synthetic approaches have been implemented to afford fluorinated organic semiconductors. In this review, we discuss some of the recent and most interesting organic semiconductors with C–F and C–CF_3 bonds as well as their application.

Keywords: fluorine, luminescence, organic semiconductor, fluorescence, TADF, OLED.

1. Introduction

The optoelectronic properties of organic semiconductive compounds are determined by the distribution of the π-electronic cloud on the molecule. Incorporation of substituents with different inductive(+*I*/-*I*) and mesomeric (+*M*/-*M*) effects into π-conjugated structures allows to alter wide variety of important properties, *i.e.*, the width of the optical band gap and the color of emission, the values of ionization potential and electron affinity, the rates of charge carrier transport, the photoluminescence quantum yield (PLQY), *etc*. Also, by careful alignment of electron-withdrawing and electron-donating fragments in the single molecule, it is possible to achieve various types of emission and, most importantly, realize full utilization of non-emissive triplet excitons and maximize the electroluminescent performance of organic light-emitting diodes (OLEDs). For example, a well-known strategy to harvest triplet excitons through thermally activated delayed fluorescence (TADF) is to design compounds with spatially separated highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO, respectively).[1] HOMOs usually situate on the fragments rich in substituents with +*I* and +*M* effects, whereas LUMOs distribute over the fragments that are characterized by –*I* and –*M*. Fluorination is a superior design strategy to form a strongly polarized C-F bond and achieve the desirable characteristics of an organic semiconductor. Fluorine, owing to its small atomic radius and strong electronegativity, can form strongly-polarized carbon-fluorine bonds and, therefore, completely alter the properties of organic compounds. The XX century gave an extreme rise to organofluorine compounds, primarily for use in pharmacology and drug design.[2–4] It is estimated that almost one-fifth of drugs introduced to the market are organofluorines.[5] Fluorine-containing compounds also find wide application in the development of functional materials,[6–8] especially plastics[9] and rechargeable batteries.[10] From the end of the XX century, with the extensive investigations of semiconductive properties of organic compounds, fluorine-containing materials have been broadly implemented in organic optoelectronics.[11] The urge to develop fully-organic semiconductors is dictated mainly by the need to decrease the usage of toxic chemicals and heavy metals that are used upon the fabrication of inorganic materials. The ease of structural modification and the cost-effectiveness of synthesis of organic compounds are nonetheless important reasons that promote research in this area. Fluorine-containing compounds are known as electron-transporters,[12] fluorescent and TADF-emitters for OLEDs,[13,14] they demonstrate efficient room temperature phosphorescence (RTP)[15] and are utilized for oxygen sensing.[16] Besides, fluorinated compounds find application as sensitizers[17] and hole-transporters for organic photovoltaics.[18]

---

[1] Department of Polymer Chemistry and Technology, Kaunas University of Technology, Baršausko 59, 51423 Kaunas, Lithuania
[2] Ivan Franko National University of Lviv, 6 Kyryla i Mefodiya St., 79020 Lviv, Ukraine
✉ juozas.grazulevicius@ktu.lt

2. Impact of Fluorine on Performance of Organic Semiconductors

The use of fluorine-containing compounds imposes a vast contribution to organic optoelectronics since it can significantly enhance the performance of π-functional materials. In particular, fluorination lowers both HOMO and LUMO of π-conjugated system, that is profitable for electron injection and allows to utilize stable cathodes with lower work function, such as aluminum instead of easily oxidizable calcium.[19] Fluorine-containing compounds can form various types of intermolecular interactions that improve their thermal stability. Moreover, because of low-lying LUMOs, fluorine-containing materials are less prone to oxidation. Incorporation of fluorines forms polar bonds and alters electron density distribution in the molecule that opens up a way for fine-tuning of optoelectronic properties. Taking simple aromatic hydrocarbon benzene and its perfluorinated analogue that have an inversed distribution of the electronic density, it was established that their quadrupole moments are opposite in sign. Benzene has a large and negative quadrupole moment of $-29.0 \cdot 10^{-40}$ cm^2, whereas the quadrupole moment of hexafluorobenzene is large and positive ($37.0 \cdot 10^{-40}$ cm^2). Hence, benzene has more expressed hole-transporting features whine perfluorobenzene can transport electrons.[20]

From the dawn of organic optoelectronics, fluorine-containing compounds have been utilized as efficient electron-transporting materials. In early 2000, Heidenhein *et al.* proposed a series of perfluorinated oligo(*p*-phenylene)-based electron-transporting materials (ETMs) to drastically improve the electron injection from the cathode into the emission layer. Among them, compound **F1** (Fig. 1) demonstrated electron mobility of $2 \cdot 10^{-3}$ cm^2/V·s at $9.4 \cdot 10^5$ V/cm electric field,[21] which is two orders of magnitude higher than that of conventional metallorganic ETM Alq$_3$. Utilizing perfluoro-*p*-sexiphenyl as ETM in OLED afforded brightness of 12 150 cd/m^2 at 13.7 V, whereas perfluoronaphtyl-appended perfluoro-*p*-tetraphenyl **F2** (Fig. 1) gave a brightness of 19 970 cd/m^2 at 10 V that were remarkable at that time.

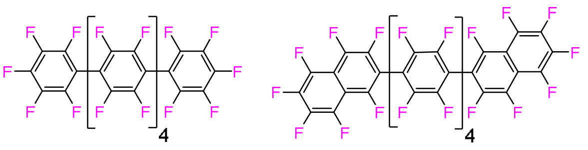

F1 **F2**

Fig. 1. Chemical structures of compounds **F1**, **F2**

Fluorination of π-functional systems is a great tool for the development of efficient TADF emitters, especially for solution-processed OLEDs, since the incorporation of fluorine atoms helps to increase the solubility and stability of organic compounds without sacrificing PLQY. The development of highly efficient solution-processed devices has been a great challenge in the research of OLEDs because the solution process has intrinsic problems to overcome, such as material incompatibility and multilayer structure formation. Notably, the general approach to enhance solution-prosessability of compound by incorporation of alkyl chains is not applicable for the design of blue emitters as it results in bathochromic shift of the emission maxima. The well-known TADF-emitter **4CzIPN** (Fig. 2), synthesized by Adachi *et al.*,[22] exhibited low performance while being utilized in solution-processed OLEDs. Cho et al. replaced one and two carbazolyl-fragments of **4CzIPN** with a fluorine electron-withdrawing unit to obtain two novel luminogens, **F3** and **F4** (**Fig. 2**), and achieved not only a superior maximum external quantum efficiency (EQE$_{max}$) of 20% for solution-processed-OLED, but also blue electroluminescence.[23] The toluene solutions of **F3** and **F4** exhibited 13% and 16% of PLQY respectively; however, after purging the solutions with N$_2$, they increased profoundly to 76% and 81%, pointing out the significant contribution of triplet excitons to the radiative transition. Both luminogens were characterized by the identical value of singlet-triplet energy splitting (ΔE_{ST}) of 0.06 eV. Host-guest mixture of SiCz:**F4** demonstrated 100% of PLQY under vacuum compared to 57% in ambient conditions, indicating the ultimate up-conversion of triplet excitons. Solution-processed OLED based on SiCz:**F4** exhibited 20% of EQE$_{max}$, with Commission Internationale de l'éclairage (CIE) colour coordinates of (0.16, 0.25) and maximum current efficiency (CE$_{max}$) of 36.1 cd/A.

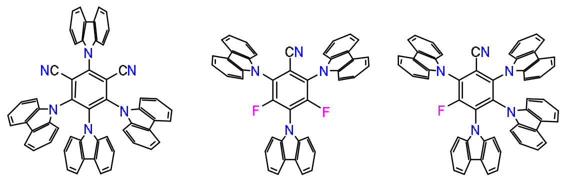
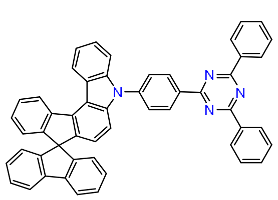

4CzIPN **F3** **F4**

Fig. 2. Chemical structures of compounds **4CzIPN**, **F3** and **F4**

Zhu *et al.* synthesized two deep-blue TADF emitters by combining a triazine electron-accepting fragment and a novel carbazole-containing spiro-type donor.[24] Phenyl linkers with (**F6**) and without (**F5**) fluorine substituent were incorporated to tune ΔE_{ST} through altering the torsion angle between acceptor and donor unities (Fig. 3). It was demonstrated that **F5** and **F6** possessed ΔE_{ST} of 0.35 and 0.24 eV. Obviously, the LUMO of **F6** was lower than that of **F5** by 0.09 eV due to the presence of an electron-withdrawing fluorine atom. Fluorine-containing **F6** possessed more rigid geometry and a larger dihedral angle between the electron-donating fragment and phenyl linker, which resulted in higher PLQY. Consequently, deep-blue OLED with CIE colour coordinates (0.16, 0.17) was fabricated utilizing **F6**:DPEPO guest-host mixture that demonstrated 7.21% of EQE, 11.16 cd/A of CE_{max} and 9.74 lm/W of maximum power efficiency (PE_{max}).


F5

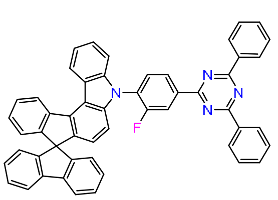
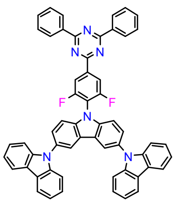
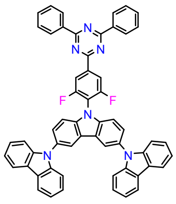

F6

Fig. 3. Chemical structures of compounds **F5** and **F6**

Upon designing TADF-luminophores, researchers often incorporate a spacer unit − usually phenyl linker, between donor and acceptor fragments, to attain some degree of spatial overlap between HOMO and LUMO that helps to increase PLQY.[25,26] When both HOMO and LUMO extend to the phenyl linker, the electronic transition from the first singlet excited state (S_1) to the ground state (S_0) adopts higher oscillator strength that provides high PLQY, since the S_1 energy is increased as a result of weakened charge-transfer (CT)-character. At the same time, the energy of the first triplet excited state (T_1) is decreased due to the prolongation of π-conjugation that results in larger ΔE_{ST} and a longer delayed component of TADF decay. Therefore, researchers try to optimize phenyl linkers through chemical modification to achieve a trade-off between high PLQY and ΔE_{ST} as negligible as possible.

One way to regulate the spatial overlap between ground and excited state wavefunctions is to introduce the steric hindrance between the linker and the donor or acceptor to partially decrease the overlap of frontier molecular orbitals (FMOs). The most common approach is the decoration of phenyl linker with one or two methyl groups in *ortho*- position to the donor or acceptor. In such a way, ΔE_{ST} is increased, and high T_1 could be realized. Instead of widely utilized CH_3- groups, Li et al. modified phenyl linkers by incorporation of fluorine atoms. They have smaller radii and afford less sterically hindered molecules. However, the electron-withdrawing effect they provide is more pronounced and has a greater influence on the CT-character of emission than methyl groups. Li et al. synthesized two TADF-agents **F7** and **F8**, which differ in the number of fluorines, in comparison with already reported compound **F9** without fluorine atoms[14] (Fig. 4). Quantum chemical calculations disclosed that the dihedral angle between phenyl linker and tercarbazole donor fragment increases with the increasing number of fluorines, and is sufficiently smaller than the one calculated for luminophores with methyl substituents. Along with increasing dihedral angle, the oscillator strength of $S_0 \rightarrow S_1$ electronic transition tends to weaken. Although both S_1 and T_1 energy values decrease from **F9** to **F8**, the S_1 value was found to be reduced more rapidly and the calculated ΔE_{ST} values decrease from 0.148 eV for **F9** to 0.055 eV for **F8**, respectively. The percentages of charge transfer for S_1 state of **F9**, **F7,** and **F8** are 78.63%, 80.20%, and 81.08%, respectively. Upon dispersion in DPEPO host the highest PLQY afforded monofluorinated compound **F7** (92%), that was followed by bi-fluorinated **F8** (84%) and dispersion of compound **F9** lacking fluorines exhibited PLQY of 84%. The EQE_{max} for devices based on compounds **F7** and **F8** were 22.5 and 19.6%, respectively, both higher than the EQE_{max} afforded by non-fluorinated **F9** (17.1%).


F7


F8

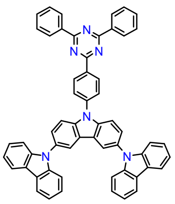

F9

Fig. 4. Chemical structures of compounds **F7-F9**

Our group extensively studied the impact of various electron-donating fragments on perfluorobiphenyl electron acceptor, which was selected due to its high value of T_1 (2.82 eV), high rates of electron transport, and ease of structural modification via nucleophilic substitution reaction. In summary, 16 compounds, **F10-F25** (Fig. 5) of donor–acceptor and donor–acceptor–donor structures were synthesized and characterized.[27–29] Films of compounds having carbazole and acridine substituents demonstrated high values of PLQY of 51%, 50%, 43%, and 46% for **F14**, **F15**, **F12,** and **F13**, respectively.[27,28] Luminophores **F10-F13**, **F17**, and **F20-F23** were characterized by negligible values of ΔE_{ST} ranging from 0.01 to 0.15 eV that promoted TADF. Other compounds possessed ΔE_{ST} values too large to afford efficient reverse intersystem crossing (rISC). All the derivatives of perfluorobiphenyl demonstrated aggregation-induced emission enhancement (AIEE) phenomenon. Interestingly, phenothiazine-containing compound **F20** was found to exist in two different types of conformers (quasi-equatorial and quasi-axial), although the existence of quasi-axial one was theoretically predicted as rather improbable[29]. In THF solutions, the high-energy conformer (quasi-axial) showed emission peaking at 514 nm, while the low-energy conformer (quasi-equatorial) showed emission peaking at 596 nm. The existence of two conformers was confirmed by time-resolved emission spectroscopy (TRES) measurements, since the emission of two different conformers was characterized by two different decays. Upon conducting AIEE experiment, the emission of only the quasi-equatorial conformer of **F20** was enhanced upon aggregation, whereas the PL intensity of the quasi-axial conformer was completely suppressed. All the compounds were isolated as crystalline substances, and differential scanning calorimetry (DSC) experiment proved their crystallinity. Interestingly, for compound **F12,** two polymorphs were detected and confirmed by the results of X-ray analysis.[27] Two polymorphs, **F12A** and **F12B,** obtained by slow evaporation from dichloromethane and isopropanol, respectively, showed emission in sky-blue and blue spectral region. The origin of emission of both polymorphs was TADF of corresponding color with PLQY of 43% and 61%. Compound **F12B** was tested in OLED with the structure TO/MoO3/NPB/**F12B**:TCz1/ TPBi/Ca/Al, where **F12B** was a part of a hybrid guest-host emissive layer to afford greenish-blue electroluminescence with EQE_{max} of 16.3% and CE_{max} of 30.8cd/A. On the contrary, compound **F15,** owing to its high energy of T_1 (3.08 eV) and high value of electron mobility ($5.1 \cdot 10^{-5}$ $\text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$), was chosen as a host for 4CzIPN[22] and DAcIPN[30] green emitters. The device with 4CzIPN:**F15** guest-host emissive layer exhibited EQE_{max} of 15.1%, CE_{max} of 45.8 cd/A and PE_{max} of 26.7 lm/W. OLED fabricated from DAcIPN demonstrated a slightly inferior performance of EQE_{max} of 10.4%, CE_{max} of 36.7 cd/A and PE_{max} of 22 lm/W, however, it afforded two-fold higher brightness (53800 cd/m^2 vs 20300 cd/m^2). Besides, owing to its TADF characteristics and sensitivity to oxygen of compound **F15**, 10 wt% solid solution of **F15** in Zeonex® was tested as an oxygen sensor[28] with Stern-Volmer constants of $6.54 \cdot 10^{-4}$ and of $7.17 \cdot 10^{-6}$ ppm^{-1}.

One of the biggest challenges in the development of organic luminophores is achieving multifunctional luminescence in a single molecule. In this case, multiple radiative pathways must be realized. Ge *et al.* synthesized unique multifunctional isomeric luminophores **F26** and **F27** (**Fig. 6**) just by appending well-known efficient TADF-emitter **DMAC-DPS** (Fig. 6) with fluorine atom in *meta-* and *ortho-* positions of the diphenylsulfone electron acceptor.[31]

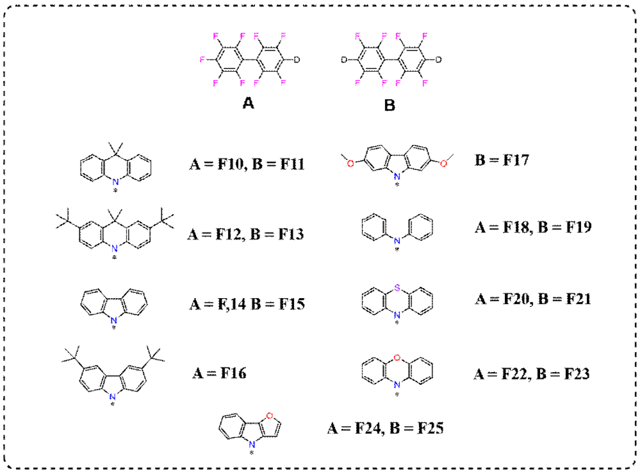


Fig. 5. Chemical structures of compounds **F10-F25**

Both compounds exhibit AIEE, mechanochromic luminescence, TADF, and RTP. Owing to the unique positioning of fluorine in **F27** that facilitates intramolecular halogen bonding between fluorine and oxygen, this compound exhibited PLQY of neat film as high as 93% in comparison to 69% and 64% of **F26** and **DMAC-DPS**. The TADF characteristics of **F27** were better due to a higher rate of rISC, in comparison with **F26** ($1.54 \cdot 10^{-6}$ s *versus* $1.06 \cdot 10^{-6}$ s). Additionally, the non-radiative rate constant of **F27** was significantly reduced in comparison with **F26** ($0.49 \cdot 10^{-5}$ s *versus* $1.44 \cdot 10^{-5}$ s), manifesting efficient utilization of excitons in **F27**. Moreover, distinct RTP emissions were observed in crystalline states for both isomers **F26** and **F27**. Crystals of **F27** showed a delayed fluorescence at 462 nm with a lifetime of 0.88 µs and phosphorescence at 476 nm with a lifetime of 8.7 ms. A similar phenomenon was detected in **F27**, with a delayed lifetime of 1.36 µs at 461 nm and a phosphorescence lifetime of 0.67 ms at 475 nm. The non-doped OLED based on **F27** as an emitter demonstrates the EQE_{max} of 21.2%, which is almost the highest EQE value among the non-doped OLEDs based on multifunctional organic TADF materials.

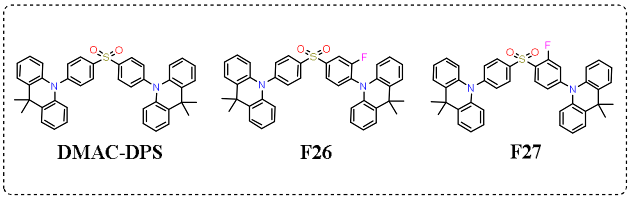


Fig. 6. Chemical structures of compounds **DMAC-DPS, F26, F27**

Trifluoromethyl aliphatic group CF_3- is of exceptional use for organic charge-transfer (CT)-luminophores to control the strength of electron-accepting part and to tune the color of emission through inductive effects. CF_3-group is not π-conjugative which makes it different from other commonly used electron-withdrawing moieties, such as -C=O, -C≡N, or $-SO_2$. The study of Yuan et al. is an illustrious example of the influence of trifluoromethyl- groups on optoelectronic properties of star-shaped TADF-luminophores **F28-F30**[32] (Fig. 7). Among them, compound **F30** having dual electron-accepting CF_3- units, demonstrated the fastest rISC with the rate of $7.02 \cdot 10^5$ s^{-1} as a consequence of smallest ΔE_{ST} value of 0.02 eV, and high PLQY close to 70%. The green host-based OLED fabricated from compound **F30** exhibited a low turn-on voltage of 2.6 V, EQE of 16.2%, PE_{max} of 40.7 lm/W and CE_{max} of 50.6 cd/A. For comparison, OLEDs based on emitters **F28** and **F29** afforded less than 1% and 9.5% of EQE_{max}, respectively.

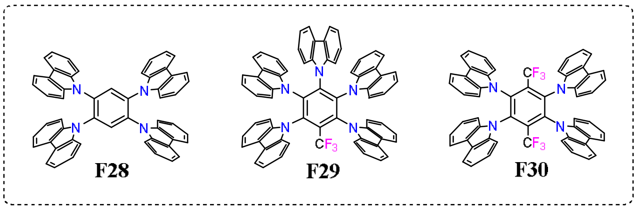

F28 **F29** **F30**

Fig. 7. Chemical structures of compounds **F28-F30**

The thorough study of Ward *et al.* disclosed that trifluoromethyl substituents differently attached to the TADF-luminophore **F31** can influence the rates of TADF through tuning of the excitonic character of the singlet and triplet excited states.[33] Based on the known efficient TADF emitter **F31**, the authors designed and synthesized four new trifluoromethyl-functionalized donor-acceptor-donor compounds **F31-F35** (Fig. 8)**.**

Changes in the orbital character of singlet and triplet states (local excitation vs. charge transfer), caused by the presence of CF_3- groups, were found to significantly influence the rates of delayed fluorescence, despite similar values of ΔE_{ST}. Additional trifluoromethyl groups significantly altered the photoluminescence characteristics of parent compound **F31.** For example, compound **F33** demonstrated a large blue shift of emission as a result of weakened donor strength. To the contrary, emission maxima of compounds **F33** and **F34** having CF_3- groups on the thioxanthene-S,S-dioxide methylene bridge, were substantially red-shifted. Interestingly, even in the bridge position, where trifluoromethyl groups are not directly attached to the aromatic rings, the acceptor strength was still significantly enhanced. Since compound **F34** has both donor and acceptor units decorated with CF_3- groups, the emission maximum was similar to that observed for unsubstituted compound **F31**.

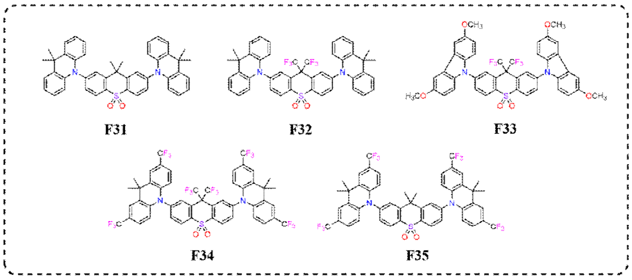
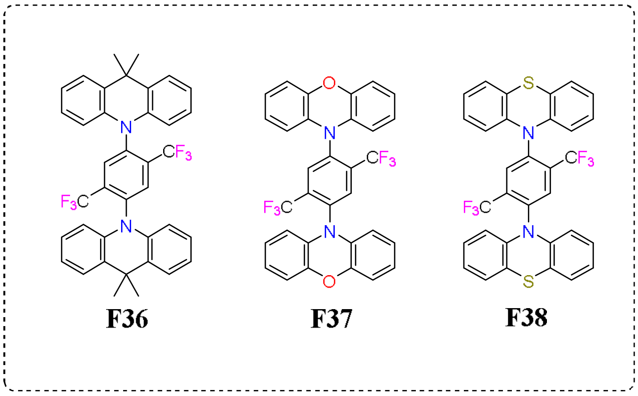

F31 **F32** **F33**
F34 **F35**

Fig. 8. Chemical structures of compounds **F31-F35**

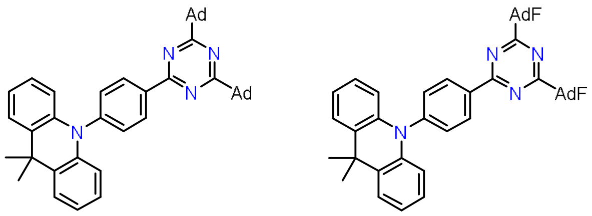
Our group recently developed three donor-acceptor-donor TADF agents **F36-F38** (Fig. 9) based on 1,4-bis(trifluoromethyl)benzene as a new acceptor.[16] Both trifluoromethyl- groups were expected to act as hydrogen bonding sites, promoting non-covalent inter- and intramolecular interactions. It is known that to achieve high internal quantum efficiency (IQE), efficient rISC between the triplet charge-transfer states (^{3}CTs) and the singlet charge-transfer states (^{1}CTs) is needed. This process is mediated by vibronic coupling between a ^{3}CT and a locally excited triplet state (^{3}LE). When the energy gap between all these three states shallows the rISC becomes faster. 1,4-Bis(trifluoromethyl)benzene, owing to its short conjugated system, has a T_1 value of 3.5 eV. Therefore, the contribution of the triplet locally excited states of the electron acceptor to the overall ^{3}LE of donor-acceptor-donor molecules was minimal. The nearly orthogonal location of donor and acceptor fragments caused strong decoupling of electrons and reduced the ΔE_{ST} value to 0.021, 0.02, and 0.011 eV for **F36**, **F37**, and **F38**, respectively. Compound **F26** showed the highest PLQY of **38**% and was used as a guest for the fabrication of OLED. The fabricated host-guest-based device emitted cyan electroluminescence with unusually stable colors at different emitter concentrations and different voltages. The efficiency at a brightness of 1000 cd/m^2 was practically the same as the maximum one due to the extremely low efficiency roll-off.



F36 **F37** **F38**

Fig. 9. Chemical structures of compounds **F36-F38**

Almost all the perfluorinated fragments used in the design of electroactive molecules are limited to trifluoromethyl groups. Recently, Akiyama et al. proposed perfluorinated adamanthyl group as a potential electron-withdrawing unit in organic electroactive materials (**F39**, Fig. 10).[34] The perfluorination of adamantane derivatives has been achieved by direct fluorination using fluorine gas in aerosol. Large adamantyl fragments are known to sufficiently increase the solubility of organic compounds through the ceasing of intermolecular interactions, which is particularly beneficial for solution-processable OLEDs. Besides, adamantlyl group has been incorporated into functional materials to broaden the energy gap and realize blue emission. On the contrary, electron-withdrawing perfluoroadamantyl can shallow the band gap, shifting the emission to the longer wavelength area. Wada *et al.* reported triazine-acridine conjugate **F40** (**Fig. 10**) decorated with two adamantly- fragments[35] to afford 22.1% EQE_{max} for blue and 11.2% for deep-blue solution-processed OLEDs. In contrast to the blue emission exhibited by **F40**, red emission was observed in **F39** as a result of the electron-withdrawing perfluoroadamantyl-group offering a deeper LUMO and a smaller HOMO–LUMO energy gap.

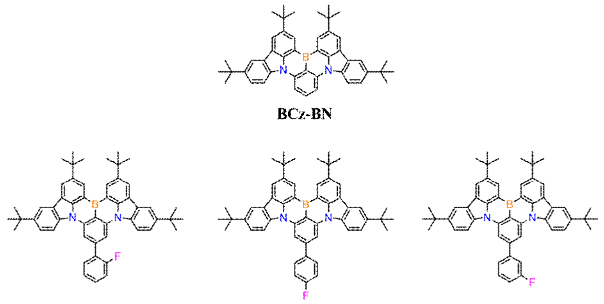


F39 **F40**

Fig. 10. Chemical structures of compounds **F39, F40**

Electroluminescence of high colour purity is one of the essential requirements for high-resolution OLED displays. It is generally known that the emission of most purely organic compounds in which 100% of IQE can be realized through harvesting of triplet excited states is characterized by quite large full-width half-maxima (FWHM, 50-100 nm) and thus low colour purity. Efficient TADF compounds are characterized by a strong CT character of emission from electron donor to electron acceptor and a large Stokes shift. The expansion of FWHM occurs as a result of vibronic coupling between the ground and excited states of the molecule. In 2016, Japanese researchers came up with the idea of molecular design boron-centered emitter DABNA, which possessed exceptional color purity and TADF properties due to the multiresonance (MR) effect, paving the way to the new class of emitters.[36] In such compounds, owing to MR of boron and nitrogen oppositely located on rigid polycyclic core, the HOMO and LUMO are located on different atoms of the same molecule. Such separation of FMOs leads to significant suppression of vibronic coupling and allows to realize emission of high color purity. Significant progress has been achieved in advances of MR-TADF emitters to narrow the emission maxima, to attain near UV/near IR[37,38] emission of high quality, and to make MR compounds solution-processable[39] and water-soluble. Particularly, the influence of a variety of different functionalities on properties of MR-TADF emitters was studied. Among them, fluorine deservers special attention.

Zhang *et al.* studied the impact of isomeric fluorophenyl-substituents on the properties of **BCz-BN**[40] (Fig. 11). Three compounds, **F41-F43,** were synthesized via Suzuki-Miayra cross-coupling reaction between isomeric fluorophenyl-boronic acid and a non-borylated MR-precursor, having a bromine atom (Fig. 9). For all the compounds the localization of HOMOs was in **BCz-BN** core whereas LUMOs were extended to the fluorophenyl functionality. As a consequence, a more prominent separation of FMOs was achieved that increased the CT-character of emission and narrowed the band gap (compared to **BCz-BN**), resulting in emission in the green spectral region. All three compounds exhibit green emission with fluorescence spectra peaked at 494 nm, 499 nm, and 496 nm for **F41**, **F42**, and **F43**, respectively. The corresponding values of FWHM were 24 nm, 24 nm, and 25 nm. The electroluminescent performance was tested in the device with hybrid emissive layers that consisted of mCPCB, 5TCzBN, and guest **F41-F43**. Narrow FWMHs of 40 nm, 38 nm, and 31 nm with electroluminescence maxima peaking at 501 nm, 499 nm, and 493 nm were recorded for OLEDs fabricated from **F41**, **F42,** and **F43**. OLED based on *meta*-isomer **F42** exhibited the highest EQE_{max} of 22.7%. The performance of other devices was slightly inferior, with 22% and 20.9% for *ortho*- and *para*-isomers **F41** and **F43**.



BCz-BN

F41 **F42** **F43**

Fig. 11. Chemical structures of compounds **Bcz-BN, F41-F43**

In 2023, the same group of researchers demonstrated that extensive fluorination of MR compounds can help to attain blue emission of exceptional color purity since fluorination lowers LUMO, thus expanding the energy gap.[41] Two boron-cored compounds were synthesized through one-shot triple borylation (Fig. 12). Notably, in the case of fluorinated compound **F44**, the yield of the reaction was significantly higher (11% *versus* 35%) since fluorines prevented borylation at unwanted sides and ceased the formation of unwanted byproducts.

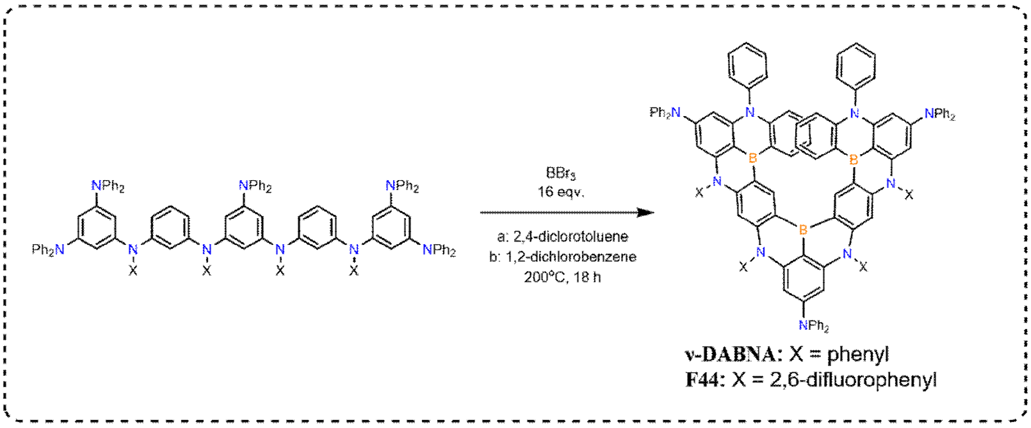


Fig. 12. Chemical structures of compounds **v-DABNA** and **F44**

Owing to –*I* effect of the fluorine atom, the emission maxima of compound **F44** is significantly blue-shifted with respect to that of **v-DABNA (**464 nm *versus* 481 nm**)**, nevertheless, the narrow FWHF of 16 nm was maintained as well as the high rate of rISC (6.5 $\times 10^5 s^{-1}$). OLED fabricated from v-DABNA as an emitter exhibited ultra-narrowband blue electroluminescence at 483 nm with a FWHM value of 17 nm and achieved a superior EQE_{max} of 26.2%, with minimum efficiency roll-offs of 0.1% and 0.9% at 100 and 1000 cd/m^2, respectively, which are record-setting values for blue MR-TADF emitters. Additionally, the device fabricated from **F44** demonstrated ultrapure deep-blue emission at 468 nm with FWHM of 15nm, which is the narrowest among the reported blue MR-TADF materials.

3. Conclusions

Fluorinated organic compounds are advantageous for a variety of applications, from drug design to functional materials, including semiconductors. There are certain benefits of fluorine atoms and fluorinated fragments for organic optoelectronics:

1. Fluorination allows to lower the values of FMOs of the molecule, which is advantageous for electron injection and allows the usage of stable cathodes with low work functions.
2. Besides good thermal and electrochemical stability, low-lying energy levels of LUMOs make fluorine-containing compounds hardly oxidizable and more chemically stable.
3. Incorporation of fluorines increases solubility and solution-processability of organic luminophores while maintaining high PLQY due to abundant non-covalent interactions.
4. Non-conjugative perfluoroalkyl groups such as trifluoromethyl, perfluoroadamantyl, and pentaluorosulfanyl are perfect unities for solution processable blue TADF-luminophores.

Significant attention should be paid to the site of functionalization since compounds varying by position of only one fluorine atom can exhibit completely different properties.

Acknowledgement

This project has received funding from the Research Council of Lithuania (LMTLT), agreement No S-LU-24-6. The authors are thankful to the Ministry of Education and Science of Ukraine and Simons Foundation (Award Number 1290588) for financial support.

List of abbreviations

+*I* – positive inductive effect
+*M* – positive mesomeric effect
AIEE – aggregation-induced emission enhancement
CE_{max} – maximum current efficiency
CIE – Commision Internationale de l’Eclaraige
CT – charge transfer
DSC – differential scanning calorimetry
EQE_{max} – maximum external quantum efficiency
etc. – et cetera
eV – electronvolt

S_1 – first singlet excited state
FMO – frontier molecular orbital
FWHM – full-width half-maxima
HOMO – highest occupied molecular orbital
-*I* – negative inductive effect
i.e. – id est
IQE – internal quantum efficiency
LUMO – lowest unoccupied molecular orbital
-*M* – negative mesomeric
MR – multiresonant
OLED – organic light-emitting diode
PE_{max} – maximum power efficiency
PLQY – photoluminescence quantum yield
ppm. – part per million
rISC – reverse intersystem crossing
RTP – room temperature phosphorescence
S_0 – ground state
T_1 – first triplet excited state
TADF – thermally activated delayed fluorescence
TRES – time-resolved emission spectroscopy
ΔE_{ST} – singlet-triplet energy splitting

References

[1] Shi, Y. Z.; Wu, H.; Wang, K.; Yu, J.; Ou, X. M.; Zhang, X. H. Recent Progress in Thermally Activated Delayed Fluorescence Emitters for Nondoped Organic Light-Emitting Diodes. *Chem. Sci.* **2022**, *13*, 3625–3651. https://doi.org/10.1039/D1SC07180G

[2] Shabir, G.; Saeed, A.; Zahid, W.; Naseer, F.; Riaz, Z.; Khalil, N.; Muneeba; Albericio, F. Chemistry and Pharmacology of Fluorinated Drugs Approved by the FDA (2016–2022). *Pharmaceuticals* **2023**, *16*, 1162. https://doi.org/10.3390/PH16081162

[3] Gillis, E. P.; Eastman, K. J.; Hill, M. D.; Donnelly, D. J.; Meanwell, N. A. Applications of Fluorine in Medicinal Chemistry. *J. Med. Chem.* **2015**, *58*, 8315–8359. https://doi.org/10.1021/acs.jmedchem.5b00258

[4] Purser, S.; Moore, P. R.; Swallow, S.; Gouverneur, V. Fluorine in Medicinal Chemistry. *Chem. Soc. Rev.* **2008**, *37*, 320–330. https://doi.org/10.1039/B610213C

[5] Han, J.; Remete, A. M.; Dobson, L. S.; Kiss, L.; Izawa, K.; Moriwaki, H.; Soloshonok, V. A.; O'Hagan, D. Next Generation Organofluorine Containing Blockbuster Drugs. *J. Fluor. Chem.* **2020**, *239*, 109639. https://doi.org/10.1016/J.JFLUCHEM.2020.109639

[6] Mukbaniani, O.; Aneli, J.; Plonska-Brzezinska, M.; Tatrishvili, T.; Markarashvili, E. Fluorine Containing Siloxane Based Polymer Electrolyte Membranes. *Chem. Chem. Technol.* **2019**, *13*, 444–450. https://doi.org/10.23939/chcht13.04.444

[7] Budnik, O.; Budnik, A.; Sviderskiy, V.; Berladir, K.; Rudenko, P. Structural Conformation of Polytetrafluoroethylene Composite Matrix. *Chem. Chem. Technol.* **2016**, *10*, 241–246. https://doi.org/10.23939/chcht10.02.241

[8] Chebotarev, A.; Demchuk, A.; Bevziuk, K.; Snigur, D. Mixed Ligand Complex of Lanthanum(III) and Alizarine-Complexone with Fluoride in Micellar Medium for Spectrophotometric Determination of Total Fluorine. *Chem. Chem. Technol.* **2020**, *14*, 1–6. https://doi.org/10.23939/chcht14.01.001

[9] Drobny, J. G. Fluorine-Containing Polymers. In *Brydson's Plastics Materials*. Eighth Ed.; Gilbert, M., Ed.; Elsevier Ltd. 2017; pp 389–425.

[10] Naren, T.; Jiang, R.; Gu, Q.; Kuang, G.; Chen, L.; Zhang, Q. Fluorinated Organic Compounds as Promising Materials to Protect Lithium Metal Anode: A Review. *Mater. Today Energy* **2024**, *40*, 101512. https://doi.org/10.1016/j.mtener.2024.101512

[11] Babudri, F.; Farinola, G. M.; Naso, F.; Ragni, R. Fluorinated Organic Materials for Electronic and Optoelectronic Applications: The Role of the Fluorine Atom. *Chem. Commun.* **2007**, 1003–1022. https://doi.org/10.1039/B611336B

[12] Burdon, J. Electron Transfer in Organic Fluorine Chemistry. *J. Fluor. Chem.* **1989**, *45*, 110. https://doi.org/10.1016/S0022-1139(00)84482-6

[13] Hong, G.; Si, C.; Gupta, A. K.; Bizzarri, C.; Nieger, M.; Samuel, I. D. W.; Zysman-Colman, E.; Bräse, S. Fluorinated Dibenzo[a,c]-Phenazine-Based Green to Red Thermally Activated Delayed Fluorescent OLED Emitters. *J. Mater. Chem. C* **2022**, *10*, 4757–4766. https://doi.org/10.1039/D1TC04918F

[14] Li, Y.; Liang, J. J.; Li, H. C.; Cui, L. S.; Fung, M. K.; Barlow, S.; Marder, S. R.; Adachi, C.; Jiang, Z. Q.; Liao, L. S. The Role of Fluorine-Substitution on the π-Bridge in Constructing Effective Thermally Activated Delayed Fluorescence Molecules. *J. Mater. Chem. C* **2018**, *6*, 5536–5541. https://doi.org/10.1039/C8TC01158C

[15] Guo, Q.; Huang, Z.; Liu, J.; Li, X.; Zheng, Y.; Gao, X.; Liu, H.; Li, J. Positional Effects of Fluorine Substitution on Room Temperature Phosphorescence in Hexaphenylmelamine Derivatives. *New J. Chem.* **2025**, *49*, 674–678. https://doi.org/10.1039/D4NJ04627G

[16] Skhirtladze, L.; Leitonas, K.; Bucinskas, A.; Woon, K. L.; Volyniuk, D.; Keruckienė, R.; Mahmoudi, M.; Lapkowski, M.; Ariffin, A.; Grazulevicius, J. V. Turn on of Room Temperature Phosphorescence of Donor-Acceptor-Donor Type Compounds via Transformation of Excited States by Rigid Hosts for Oxygen Sensing. *Sensors Actuators B Chem.* **2023**, *380*, 133295. https://doi.org/10.1016/J.SNB.2023.133295

[17] Lee, M. W.; Kim, J. Y.; Ko, M. J. Enhanced Photovoltaic Performance of D-π-A Organic Sensitizers by Simple Fluorination of Acceptor Unit. *Org. Electron.* **2022**, *108*, 106606. https://doi.org/10.1016/J.ORGEL.2022.106606.

[18] Chen, J.; Zhu, X.; Zhang, J.; Wei, L. Fluorinated Hole Transport Material Resistant to High Annealing Temperature Applied in Inverted Perovskites Solar Cells. *Synth. Met.* **2024**, *306*, 117647. https://doi.org/10.1016/J.SYNTHMET.2024.117647

[19] Stössel, M.; Staudigel, J.; Steuber, F.; Simmerer, J.; Winnacker, A. Impact of the Cathode Metal Work Function on the Performance of Vacuum-Deposited Organic Light Emitting-Devices. *Appl. Phys. A* **1999**, *68*, 387–390. https://doi.org/10.1007/S003390050910

[20] Battaglia, M. R.; Buckingham, A. D.; Williams, J. H. The Electric Quadrupole Moments of Benzene and Hexafluorobenzene. *Chem. Phys. Lett.* **1981**, *78*, 421–423. https://doi.org/10.1016/0009-2614(81)85228-1

[21] Heidenhain, S. B.; Sakamoto, Y.; Suzuki, T.; Miura, A.; Fujikawa, H.; Mori, T.; Tokito, S.; Taga, Y. Perfluorinated Oligo(*p*-Phenylene)s: Efficient n-Type Semiconductors for Organic Light-Emitting Diodes. *J. Am. Chem. Soc.* **2000**, *122*, 10240–10241. https://doi.org/10.1021/ja002309o

[22] Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly Efficient Organic Light-Emitting Diodes from Delayed Fluorescence. *Nature* **2012**, *492*, 234–238. https://doi.org/10.1038/nature11687

[23] Cho, Y. J.; Chin, B. D.; Jeon, S. K.; Lee, J. Y. 20% External Quantum Efficiency in Solution-Processed Blue Thermally Activated

Delayed Fluorescent Devices. *Adv. Funct. Mater*. **2015**, *25*, 6786–6792. https://doi.org/10.1002/ADFM.201502995

[24] Zhu, X. D.; Tian, Q. S.; Zheng, Q.; Wang, Y. K.; Yuan, Y.; Li, Y.; Jiang, Z. Q.; Liao, L. S. Deep-Blue Thermally Activated Delayed Fluorescence Materials with High Glass Transition Temperature. *J. Lumin*. **2019**, *206*, 146–153. https://doi.org/10.1016/J.JLUMIN.2018.10.017

[25] Hussain, A.; Kanwal, F.; Irfan, A.; Hassan, M.; Zhang, J. Exploring the Influence of Engineering the Linker between the Donor and Acceptor Fragments on Thermally Activated Delayed Fluorescence Characteristics. *ACS Omega* **2023**, *8*, 15638–15649. https://doi.org/10.1021/acsomega.3c01098

[26] Paras; Ramachandran, C. N. Tuning of the Singlet–Triplet Energy Gap of Donor-Linker-Acceptor Based Thermally Activated Delayed Fluorescent Emitters. *J. Fluoresc*. **2024**, *34*, 1343–1351. https://doi.org/10.1007/S10895-023-03365-2/FIGURES/3

[27] Hladka, I.; Volyniuk, D.; Bezvikonnyi, O.; Kinzhybalo, V.; Bednarchuk, T. J.; Danyliv, Y.; Lytvyn, R.; Lazauskas, A.; Grazulevicius, J. V. Polymorphism of Derivatives of *tert*-Butyl Substituted Acridan and Perfluorobiphenyl as Sky-Blue OLED Emitters Exhibiting Aggregation Induced Thermally Activated Delayed Fluorescence. *J. Mater. Chem. C* **2018**, *6*, 13179–13189. https://doi.org/10.1039/C8TC04867C

[28] Danyliv, I.; Danyliv, Y.; Lytvyn, R.; Bezvikonnyi, O.; Volyniuk, D.; Simokaitiene, J.; Ivaniuk, K.; Tsiko, U.; Tomkeviciene, A.; Dabulienė, A.; *et al*. Multifunctional Derivatives of Donor-Substituted Perfluorobiphenyl for OLEDs and Optical Oxygen Sensors. *Dye. Pigment*. **2021**, *193*, 109493. https://doi.org/10.1016/J.DYEPIG.2021.109493

[29] Danyliv, I.; Danyliv, Y.; Stanitska, M.; Bezvikonnyi, O.; Volyniuk, D.; Lytvyn, R.; Horak, Y.; Matulis, V.; Lyakhov, D.; Michels, D.; et al. Effects of the Nature of Donor Substituents on the Photophysical and Electroluminescence Properties of Derivatives of Perfluorobiphenyl: Donor-Acceptor versus Donor-Acceptor-Donor Type AIEE/TADF Emitters. *J. Mater. Chem. C* **2024**, *12*, 2911–2925. https://doi.org/10.1039/D3TC04633H

[30] Skuodis, E.; Bezvikonnyi, O.; Tomkeviciene, A.; Volyniuk, D.; Mimaite, V.; Lazauskas, A.; Bucinskas, A.; Keruckiene, R.; Sini, G.; Grazulevicius, J. V. Aggregation, Thermal Annealing, and Hosting Effects on Performances of an Acridan-Based TADF Emitter. *Org. Electron*. **2018**, *63*, 29–40. https://doi.org/10.1016/J.ORGEL.2018.09.002

[31] Ge, X.; Li, G.; Guo, D.; Yang, Z.; Mao, Z.; Zhao, J.; Chi, Z. A Strategy for Designing Multifunctional TADF Materials for High-Performance Non-Doped OLEDs by Intramolecular Halogen Bonding. *Adv. Opt. Mater*. **2024**, *12*, 2302535. https://doi.org/10.1002/ADOM.202302535.

[32] Yuan, W.; Jin, G.; Su, N.; Hu, D.; Shi, W.; Zheng, Y. X.; Tao, Y. The Electron Inductive Effect of Dual Non-Conjugated Trifluoromethyl Acceptors for Highly Efficient Thermally Activated Delayed Fluorescence OLEDs. *Dye. Pigment*. **2020**, *183*, 108705. https://doi.org/10.1016/J.DYEPIG.2020.108705

[33] Ward, J. S.; Danos, A.; Stachelek, P.; Fox, M. A.; Batsanov, A. S.; Monkman, A. P.; Bryce, M. R. Exploiting Trifluoromethyl Substituents for Tuning Orbital Character of Singlet and Triplet States to Increase the Rate of Thermally Activated Delayed Fluorescence. *Mater. Chem. Front*. **2020**, *4*, 3602–3615. https://doi.org/10.1039/D0QM00429D

[34] Akiyama, M.; Yasuda, Y.; Kisoi, D.; Kusakabe, Y.; Kaji, H.; Imahori, H. The Perfluoroadamantyl Group: A Bulky and Highly Electron-Withdrawing Substituent in Thermally Activated Delayed Fluorescence Materials. *Bull. Chem. Soc. Jpn*. **2024**, *97*, uoae025. https://doi.org/10.1093/BULCSJ/UOAE025

[35] Wada, Y.; Kubo, S.; Kaji, H.; Wada, Y.; Kubo, S.; Kaji, H. Adamantyl Substitution Strategy for Realizing Solution-Processable Thermally Stable Deep-Blue Thermally Activated Delayed Fluorescence Materials. *Adv. Mater*. **2018**, *30*, 1705641. https://doi.org/10.1002/ADMA.201705641.

[36] Hatakeyama, T.; Shiren, K.; Nakajima, K.; Nomura, S.; Nakatsuka, S.; Kinoshita, K.; Ni, J.; Ono, Y.; Ikuta Hatakeyama, T. T.; Nakajima, K.; *et al*. Ultrapure Blue Thermally Activated Delayed Fluorescence Molecules: Efficient HOMO–LUMO Separation by the Multiple Resonance Effect. *Adv. Mater*. **2016**, *28*, 2777–2781. https://doi.org/10.1002/ADMA.201505491

[37] Wu, S.; Zhang, L.; Wang, J.; Kumar Gupta, A.; Samuel, I. D. W.; Zysman-Colman, E. Merging Boron and Carbonyl Based MR-TADF Emitter Designs to Achieve High Performance Pure Blue OLEDs**. *Angew. Chemie Int. Ed*. **2023**, *62*, e202305182. https://doi.org/10.1002/ANIE.202305182

[38] Hua, T.; Li, N.; Huang, Z.; Zhang, Y.; Wang, L.; Chen, Z.; Miao, J.; Cao, X.; Wang, X.; Yang, C. Narrowband Near-Infrared Multiple-Resonance Thermally Activated Delayed Fluorescence Emitters towards High-Performance and Stable Organic Light-Emitting Diodes. *Angew. Chemie Int. Ed.* **2024**, *63*, e202318433. https://doi.org/10.1002/ANIE.202318433

[39] Cai, X.; Xu, Y.; Pan, Y.; Li, L.; Pu, Y.; Zhuang, X.; Li, C.; Wang, Y. Solution-Processable Pure-Red Multiple Resonance-Induced Thermally Activated Delayed Fluorescence Emitter for Organic Light-Emitting Diode with External Quantum Efficiency over 20 %. *Angew. Chemie Int. Ed.* **2023**, *62*, e202216473. https://doi.org/10.1002/ANIE.202216473

[40] Zhang, Y.; Zhang, D.; Wei, J.; Liu, Z.; Lu, Y.; Duan, L. Multi-Resonance Induced Thermally Activated Delayed Fluorophores for Narrowband Green OLEDs. *Angew. Chemie* **2019**, *131*, 17068–17073. https://doi.org/10.1002/ANGE.201911266

[41] Oda, S.; Kawakami, B.; Horiuchi, M.; Yamasaki, Y.; Kawasumi, R.; Hatakeyama, T. Ultra-Narrowband Blue Multi-Resonance Thermally Activated Delayed Fluorescence Materials. *Adv. Sci*. **2023**, *10*, 2205070. https://doi.org/10.1002/ADVS.202205070

Received: January 20, 2025 / Revised: February 24, 2025 / Accepted: March 01, 2025

МОДИФІКАЦІЯ ФТОРОМ ЯК ЕФЕКТИВНИЙ СПОСІБ ПОКРАЩЕННЯ ХАРАКТЕРИСТИК ОРГАНІЧНИХ ЕЛЕКТРОАКТИВНИХ СПОЛУК (ОГЛЯД)

Анотація. *Функціоналізація органічних напівпровідників атомами фтору та фторовмісними групами може розширити спектр їхніх властивостей: збільшити швидкість транспорту електронів, індукувати залучення темнових триплетних екситонів до емісії через термічно активовану уповільнену флуоресценцію (TADF) або фосфоресценцію за кімнатної температури (RTP), покращити квантовий вихід фотолюмінесценції (PLQY) через формування множинних внутрішньо- та міжмолекулярних взаємодій, підвищити технологічність сполук і, відповідно, знизити вартість виготовлення пристроїв. Для отримання фторовмісних органічних напівпровідників були реалізовані різноманітні синтетичні підходи. У цьому огляді йдеться про деякі з останніх і найцікавіших органічних напівпровідників із зв'язками C–F і C–CF*$_3$ *та про їхнє застосування.*

Ключові слова: *фтор, люмінесценція, органічні напівпровідники, флуоресценція, TADF, OLED.*