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## White hyperelectrofluorescence from solution-processable OLEDs based on phenothiazine substituted tetraphenylethylene derivatives

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### Abstract

Mechanochromic emitters with appropriate combination of properties for white hyperfluorescent solution-processable organic light emitting diodes (OLEDs) were developed involving phenothiazine, tetraphenylethylene, and electron withdrawing (cyano (-CN)) or phenyl acrylonitrile (-CHC(CN)Ph) groups. Among four studied compounds, the best performance in white hyperfluorescence OLEDs was shown by one compound (named **PTZTPE-3**) due to its orange emission with high photoluminescence quantum yield of 66% observed for toluene solution and of 39% for doped films, low-dispersity hole-transporting properties, appropriate ionization potential (5.5 eV) and electron affinity (3.24 eV). The perfect combination of these characteristics is required for efficient white hyperfluorescence. Mechanoluminescent properties with hypsochromically shifted emission under external stimuli were additionally detected and studied in detail for the developed **PTZTPE** compounds discovering their multifunctionality for either sensing, imaging, security, memory or other proposes. Using **PTZTPE** compounds hyperfluorescence systems were developed and utilized in simply processed white organic light-emitting diodes involving conventional host, host with thermally activated delayed fluorescence

(TADF) properties and singlet emitters. Due to the Förster resonance energy transfer from co-hosts to blue and orange emitters, the hyperfluorescence based white OLEDs were developed. They were characterized by high quality of white electroluminescence with color rendering index of 67 and CIE1931 color coordinates of (0.28, 0.38), in the best case. The maximum external quantum efficiency (8.2%) of the solution-processed OLED was higher than the theoretical limit (5–7.5%) of the devices based on the conventional fluorescent emitters.

### Introduction

Organic small molecules with intense solid state emission have attracted considerable research interest on account of their promising applications in the field of data storage devices, organic light emitting diodes (OLEDs), security inks, solid state lasers and non-linear optics (NLO)  $^{[1-9]}$ . The change of emission wavelength in response to mechanical stimuli such as smearing, mechanical pressure, stretching, shearing etc. is called mechanofluorochromism (MFC) [10-14]. To date, only a few molecules have been reported which exhibit hypsochromically shifted emission in response to mechanical grinding <sup>[15-17]</sup>. It is widely accepted that the solid state optical properties of MFC materials is strongly depend on the molecular packing arrangements hence by regulating the intermolecular interactions, molecular conformation and packing modes between the molecules it is possible to tune the optical properties of MFC materials.<sup>[18-20]</sup> The PTZTPE-1 and PTZTPE-4 showed bathochromic shift in their emission on grinding with mortar and pestle which was reported earlier.<sup>[21]</sup> In order to tune the molecular packing arrangements, the molecular structure of PTZTPE-1 was extended by cyano and phenyl acrylonitrile moieties to synthesize PTZTPE-2 and PTZTPE-3 (Figure 1a). The single crystal X-ray analysis reveals that the presence of electron withdrawing substituents affect the intermolecular interactions and hence resulted in more versatile mechanochromic properties of PTZTPE-2 and PTZTPE-3. The cyano group bearing

derivative (**PTZTPE-2**) shifts its emission hypsochromically on mechanical grinding while the phenyl acrylonitrile group bearing derivative (**PTZTPE-3**) shows a small hypsochromic shift in its emission and then emission shifts to longer wavelength on strong grinding. On one hand, this result on hypsochromic shift of emission of **PTZTPE-3** predictively has potential to expand applicability of phenothiazine based tetraphenylethylene derivatives as optical functional materials for either sensing, imaging, security, memory or other proposes.



**Figure 1** (a) Chemical structures of **PTZTPE 1–4** and (b) Schematical visualization of the proposed approach for white hyperelectrofluorescence based on compound **PTZTPE-3**.

On the other hand, applicability of compounds **PTZTPE 1–4** as electronic functional materials for OLEDs was additionally studied. According to the spin statistics, positively charged hole and negatively charged electron annihilate forming one singlet exciton for every three triplet excitons. It is schematically shown as formation 25% singlets and 75% triplets in Figure 1b during the process of hole and electron recombination in organic semiconductor materials <sup>[22]</sup>. Because of that, maximum internal quantum efficiency for OLEDs based on conventional fluorescent emitters is limited to 25%, while, external quantum efficiency (EQE) is limited to 5–7.5% even if emitters are characterized by photoluminescence quantum yield (PLQY) of 100% <sup>[23]</sup>. In order to overcome this limitation, several approaches for efficient harvesting of triplet excitons were proposed. The

most well-established route is a usage of phosphorescent emitters <sup>[24]</sup>. These emitters contain heavy metal atoms (e.g., Ir and Pt) which form strong spin-orbit interaction determinant very efficient intersystem crossing (ISC). Because of that, these compounds can radiatively harvest triplet excitons ensuring 100% internal quantum efficiency of OLEDs <sup>[25,26]</sup>. Moreover, such phosphorescent emitters can be used as triplet sensitizers for fluorescent emitters yielding internal quantum efficiency of 45% under electrical excitation <sup>[27,28]</sup>. Unfortunately, organometallic systems have some intrinsic problems, such as toxicity and instability in aqueous environments <sup>[29]</sup>. An alternative route to generate additional singlet excitons is triplet-triplet annihilation (TTA) <sup>[30,31]</sup>. However, only 50% of triplet excitons can be converted into singlets which results in theoretical limit of internal quantum efficiency of 62.5% <sup>[32]</sup>. Another way to harvest triplet excitons is to employ thermally activated delayed fluorescence (TADF)<sup>[33]</sup>. TADF is based on reverse intersystem crossing (RISC) which is allowed by small difference between the first excited singlet and triplet energy levels. During RISC triplet excitons are converted into singlets recombining in radiative way. Therefore, purely organic TADF molecules enable to achieve up to 100% internal quantum efficiency under electrical excitation and at the same time allow to avoid disadvantages of phosphorescent emitters <sup>[34]</sup>. It should be noted that TADF emitters usually face the same challenges as phosphorescent emitters such as poor lifetime (mainly for blue) and broad electroluminescence spectra of TADF based OLEDs <sup>[35]</sup>.

Recent approach for efficient harvesting of triplet excitons in OLEDs is hyperfluorescence which theoretically allows to achieve internal quantum efficiency of 100% <sup>[36]</sup>. In all organic hyperfluorescence systems, TADF molecules are employed as assistant dopants (co-hosts) in fluorescent dopants and wide bandgap host systems solving several problems at the same time <sup>[37,38]</sup>. In comparison to conventional fluorescene, hyperfluorescence suggests higher internal

quantum efficiencies and higher EQE of OLEDs. In comparison to TADF systems, hyperfluorescence based systems allow to achieve higher color purity and, more importantly, higher operational stability of OLEDs.

Mechanism of hyperfluorescence consist of several main steps <sup>[29-31]</sup> (Figure 1b). Firstly, the injected charge carriers are transported in the wide band gap conventional host. Then, injected holes and electrons are eventually trapped on co-host (TADF molecule) if its HOMO is shallower and LUMO is deeper compared with those of the conventional host material. In the third step, triplet excitons created on TADF co-host can be converted into singlet excitons via RISC. In the next step, singlet excitons of TADF host are transferred to the singlet state of conventional fluorescence emitter via Förster resonance energy transfer (FRET). Finally, efficient radiative decay from singlet level of the fluorescent emitter can be achieved. In order to construct an efficient hyperfluorescence organic systems, at least the following requirements have to be fulfilled for the selection of its components (host, TADF co-host and fluorescent emitter) <sup>[29-31]</sup>:

- Lower HOMO and higher LUMO of host than those of the TADF co-host; TADF co-host has to have wider energy gap then those of fluorescent emitter (Figure 1b). Selection of host materials with high HOMO level is critical.
- To ensure efficient FRET, the ground state absorption of fluorescent emitter and emission of TADF co-host have to be characterized by big spectral overlap.
- To avoid direct charge carriers trapping on the fluorescent emitter, low its doping concentrations (0.5–2%) and much higher concentrations of TADF co-host (10–50%) have to be selected.
- To ensure short delayed lifetime of the TADF co-host, the selected TADF molecules should be characterized by high RISC rate.

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Taking into account, to the above requirements, **PTZTPE 1–4** based hyperfluorescence systems were developed. In design strategy of such emitters, well-known aggregation induced emission (AIE)-active tetraphenylethylene (TPE) moiety and strong electron donor phenothiazine (PTZ) unit were involved. To tune their energy levels, additional substitution by different electron withdrawing group was exploited. Thus, we have synthesized two derivatives of PTZ and TPE (PTZTPE-2 and PTZTPE-3) in which the PTZ moiety contains TPE unit on one side and an electron withdrawing group on the other side. 1,3-Bis(N-carbazolyl)benzene (mCP) <sup>[39,40]</sup> was the conventional host and 4,4'-(9H,9'H-[3,3'-bicarbazole]-9,9'-diyl)bis(3selected as (trifluoromethyl)benzonitrile) (pCNBCzoCF<sub>3</sub>) <sup>[41-43]</sup> as TADF co-host. Despite the fact that hyperfluorescence is mainly used to improve EQE of single-color fluorescent OLEDs, it can be also employed to construct white OLEDs <sup>[44,45]</sup>. Most of the reported hyperfluorescence-based WOLEDs contain single emission layer with two fluorescent emitters [46]. In this study we propose new approach for the design of solution-processable white hyperfluorescent OLEDs using two separate blue and orange emitting layers (Figure 1b). In the developed device structure, the holeelectron pairs recombine within the orange light-emitting layer on mCP and pCNBCzoCF<sub>3</sub> cohosts forming 25% of singlet excitons and 75% of triplet excitons. Then, triplets can be converted to singlets due to RISC of TADF co-host. In the same time, singlets can be transferred from cohosts mCP and pCNBCzoCF<sub>3</sub> to conventional blue and orange emitters via FRET since there is overlapping between emission spectra of co-hosts and absorption spectrum of emitters as well as there is small enough distance between sensitizing co-hosts and emitters for the long-range FRET (up to ca. 8.5 nm) <sup>[47]</sup>. These processes in the proposed structure result in white hyperelectroluminescence with theoretical internal quantum efficiency of 100% because of harvesting of triplets via TADF. For the optimized devices based on blue poly(9,9-dioctylfluorene-

alt-N-(4-sec-butylphenyl)-diphenylamine) (TFB) and orange **PTZTPE-3** emitters, white hyperelectrofluorescence with external quantum efficiency of 8.2%, CIE color coordinate of (0.28, 0.38) and color rendering index of 67 were achieved.

### **Results and discussion**

The synthetic route for the target compounds (**PTZTPE-2** and **PTZTPE-3**) is outlined in Scheme 1. The reaction of 4-(1,2,2-triphenylvinyl)-phenylboronic acid pinacol ester (**TPE-Bpin**) with 7-bromo-10-propyl-10H-phenothiazine-3-carbonitrile (**5**) was carried out by Pd-catalyzed Suzuki cross coupling reaction to furnish **PTZTPE-2** in 78% yield. The **TPE-Bpin** when reacted with 2-phenyl-3-(10-propyl-10H-phenothiazin-3-yl)acrylonitrile (**6**), it resulted in the formation of a mixture of the *E* and *Z* isomers of **PTZTPE-3** in 69% yield. Due to almost negligible polarity difference between the *E* and *Z* isomeric forms of **PTZTPE-3**, we tried several attempts but could not separate them into individual isomers. The detailed synthetic procedure for the intermediates involved is illustrated in scheme S1. The crystalline samples of **PTZTPE-2** were obtained by vapor diffusion method using n-pentane/dichloromethane binary solvent system and for **PTZTPE-3**, the crystalline samples was prepared by recrystallization from dichloromethane and n-hexane. The chemical structures of newly synthesized compounds **PTZTPE-2** and **PTZTPE-3** were well characterized by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, high resolution mass spectrometry and single crystal XRD techniques.

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Scheme 1. Synthetic scheme for PTZTPE-2 and PTZTPE-3.

### **Photophysical properties**

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The electronic absorption and emission spectra of **PTZTPE-2** and **PTZTPE-3** are depicted in Figure 2 and the corresponding data are illustrated in Table 1. The absorption spectra of **PTZTPE-2** and **PTZTPE-3** in THF solution  $(1\times10^{-5} \text{ M})$  display a sharp absorption band in shorter wavelength region at 280 nm and 304 nm, respectively, which could be attributed to the  $\pi$ - $\pi$ \* transitions and a charge transfer (CT) band in longer wavelength region was observed at 322 nm and 423 nm for **PTZTPE-2** and **PTZTPE-3**, respectively. The CT nature of absorption peak was then examined by solvatochromism. The solvatochromic nature of fluorescence of **PTZTPE-2** and **PTZTPE-3** reveals stronger donor acceptor character of **PTZTPE-3** compared to **PTZTPE-2**. The **PTZTPE-3** exhibits 101 nm red shifted absorption compared to **PTZTPE-2**. Normally, TPE derivatives are non-emissive in solution due to the non-radiative energy loss of excited states by the free rotation of TPE phenyl rings but the electron withdrawing moieties bearing phenothiazine substituted derivatives of TPE (**PTZTPE-2** and **PTZTPE-3**) are emissive even in solutions.



**Figure 2** (a) Absorption and (b) normalized emission spectra of the solutions of compounds **PTZTPE-2** and **PTZTPE-3** in THF (1 x 10<sup>-5</sup> M) ( $\lambda_{exc}$  = 350 nm and 440 nm for **PTZTPE-2** and **PTZTPE-3** respectively) (c) Emission spectra of compounds **PTZTPE-2** and **PTZTPE-3** in different THF- water mixtures. (d) Plot of fluorescence intensity Vs. % of water fraction for the compounds **PTZTPE-2** and **PTZTPE-3**.

 $\Phi_{f}^{c}$ 

0.290

0.273

08

Compounds $\lambda_{abs}$ (nm), $\varepsilon$ (Lmol <sup>-1</sup> cm <sup>-1</sup> ) <sup>a</sup>		λ <sub>em</sub> (nm) <sup>a</sup>	Stokes shift (cm <sup>-1</sup> )	Δλ <sub>em</sub> <sup>b</sup> (nm)
PTZTPE-2	280 (50600), 322 (23350)	482	10309	35

 Table 1. Photophysical properties of PTZTPE-2 and PTZTPE-3.

304 (30200), 423 (10250)

**PTZTPE-3** 

<sup>a</sup> Recorded in dry THF (1 x 10 <sup>-5</sup> M concentration). <sup>b</sup> difference of the emission maxima in the crystalline state and in solution, <sup>c</sup> fluorescence quantum yields were measured using quinine sulphate as a standard in 0.5 M $H_2SO_4$ solution for <b>PTZTPE-2</b> and rhodamine-6G as standard in ethanol for
<sup>a</sup> Recorded in dry THF (1 x 10 <sup>-5</sup> M concentration). <sup>b</sup> difference of the emission maxima in the crystalline state and in solution, <sup>c</sup> fluorescence quantum yields were measured using quinine sulphate
<sup>a</sup> Recorded in dry THF (1 x 10 <sup>-5</sup> M concentration). <sup>b</sup> difference of the emission maxima in the

585

6547

In case of compound **PTZTPE-2**, PL spectra at similar wavelengths were recorded for its THF solution and for the dispersions in THF:water mixtures with the different fractions of water ( $f_w$ ) (Figure 2c). At water fractions ranging from 30 to 85%, PL intensity constantly increased with the increase of water fraction due to the formation of **PTZTPE-2** aggregates (Figure 2d). This result is related to AIE effect caused by TPE group. At  $f_w$  above 85%, PL intensity of the dispersions in THF:water mixtures of **PTZTPE-2** decreased. This observation can be explained by precipitation of heavy **PTZTPE-2** aggregates but not by any kind of aggregation-induced quenching. In case of compound **PTZTPE-3**, PL spectra of its dispersions in THF:water mixtures PL intensity decreased the spectra red-shifted when water fractions were changed from 0% to 50%. When aggregates started to grow due to poor solubility of **PTZTPE-3** in water ( $f_w > 50\%$ ), PL intensity of the corresponding mixtures increased demonstrating AIE effect. Different PL spectra and PL intensity trends of the dispersions of **PTZTPE-2** and **PTZTPE-3** in THF:water mixtures result from their different solvatochromism which is discussed in the next section.

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### Solvatochromism

The effect of polarity of different solvents on the absorption and emission spectra of **PTZTPE-2** and **PTZTPE-3** was investigated and the results are shown in Figure S1, Figure 3 and Table S1. On increasing polarity of the solvents, the **PTZTPE-2** and **PTZTPE-3** do not show much variation in their absorption spectra but their emission spectra show remarkable bathochromic shifts. This is because polar solvents stabilize the excited states more than the ground states which results in decrease in the energy of excited states. In non-polar solvents such as toluene, the emission peak of **PTZTPE-2** and **PTZTPE-3** was centered at 480 nm (blue) and 563 nm (yellow), respectively. With increasing polarity, the emission spectra show bathochromic shift and in polar solvent such as DMF the emission peak was observed at 492 nm (cyan) and 613 nm (red) for **PTZTPE-2** and **PTZTPE-3**, respectively. The emission spectra of **PTZTPE-3** shows large red shift and significant color change (Figure 3 and Figure S2) compared to **PTZTPE-2** as the solvent was changed from toluene to DMF indicating better D-A character in former.



**Figure 3** Emission spectra of compounds (a) **PTZTPE-2** and (b) **PTZTPE-3** in solvents of different polarity. (excitation wavelength for **PTZTPE-2** and **PTZTPE-3** is 350 nm and 440 nm respectively).

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### **Computational analysis**

In a view to get insight of the molecular geometries and to evaluate the electron density distribution, the ground state optimization of the PTZTPE-2 and PTZTPE-3 was carried out using the basis set B3LYP/6-31G(d,p) <sup>[48-50]</sup>. The frontier orbitals of **PTZTPE-2** and **PTZTPE-3** are shown in Figure S5 and the corresponding data are listed in Table S4. The optimized molecular structures of PTZTPE-2 and PTZTPE-3 show bent shape for phenothiazine. The TPE phenyl ring and the PTZ moiety has a dihedral angle of 37.58° and 35.69° in PTZTPE-2 and PTZTPE-3, respectively. The molecular orbital of PTZTPE-2 shows that the electronic density of both the HOMO state and the LUMO state is localized over the entire molecular framework, while for **PTZTPE-3**, the electronic density of the HOMO state is concentrated on the phenothiazine moiety and that of the LUMO state is stretched towards the phenyl acrylonitrile moiety. The separation of electron density on HOMO-LUMO energy levels suggested that the PTZTPE-3 has better D-A character compared to PTZTPE-2. The HOMO-LUMO gap values were calculated for PTZTPE-2 and PTZTPE-3 which is found to be 3.75 eV and 2.99 eV, respectively. Furthermore, the time dependent density functional theory (TD-DFT) calculations were done using B3LYP/6-31G(d,p) level to study the excited state energies and transitions. The transitions with composition, oscillator strength and assignments are shown in Table S3.

### Mechanochromism

The mechanochromic properties of **PTZTPE-2** and **PTZTPE-3** were explored by grinding the crystalline samples in mortar with a pestle. The solid-state emission spectra of **PTZTPE-2** and **PTZTPE-3** under various external stimuli are shown in Figure 4 and the related data are listed in Table S5. The study shows that the **PTZTPE-2** and **PTZTPE-3** exhibit substituent dependent mechanochromic properties. Earlier, we have reported the mechanochromic properties of

**PTZTPE-1** and **PTZTPE-4** in which both the synthesized derivatives upon mechanical grinding shift their emission to longer wavelength region with a spectral shift of +44 nm and +47 nm, respectively.<sup>[21]</sup> In this work, the incorporation of cyano and phenyl acrylonitrile moieties affects the intermolecular interactions and hence resulted in more versatile mechanochromic properties of **PTZTPE-2** and **PTZTPE-3**. The pristine form of **PTZTPE-2** was ground mechanically using mortar and pestle and the solid-state emission spectra was recorded using fluorescence spectroscopy. On grinding, the **PTZTPE-2** hypsochromically shifts its emission from 517 nm to 489 nm and shows grinding induced spectral shift ( $\Delta\lambda$ ) of -28 nm. On fuming the ground sample of **PTZTPE-2** with dichloromethane for about 5–6 minutes, the emission spectra shift to 512 nm. The powder XRD analysis were carried out for the pristine, ground and fumed samples of **PTZTPE-2** which shows that the spectral shift is associated with the phase transformation from the crystalline to amorphous state. On the other hand, the PTZTPE-3 shows different mechanochromic phenomena upon gentle grinding and strong grinding. The crystalline form of **PTZTPE-3** was considered as pristine-o form which is orange in color and emits at 593 nm. Gentle grinding of pristine-o form of **PTZTPE-3** hypsochromically shifted its emission to 590 nm ( $\Delta\lambda$  = -3 nm) and shows yellow emission. The yellow form of **PTZTPE-3** was considered as pristine-y form which on strong grinding, bathochromically shifts its emission to 611 nm and shows grinding induced spectral shift ( $\Delta\lambda$ ) of +21 nm. The pristine-y form was not stable, and it reversibly converts to the pristine-o form within a very short period of time hence we were not able to characterize the pristine-y form but the small blue shift observed on gentle grinding could be explained on the basis of results obtained from single crystal X-ray analysis which reveals that the pristine-o form contains a dimeric unit of **PTZTPE-3** molecules in which the S atom of phenothiazine of one **PTZTPE-3** molecule interacts with the CN group of a neighbouring **PTZTPE-3** molecule through

C(9)-N(2)...S(1) interaction. On gentle grinding the pristine-o form of **PTZTPE-3**, the intermolecular CN...S interaction is likely to be destroyed which causes disruption of the dimeric structure resulting in a small hypsochromic shifted band <sup>[16]</sup>. The self-reformation of these dimeric interactions converts the pristine-y form again to pristine-o form. The ground sample of PTZTPE-3 when fumed with dichloromethane for about 5-6 minutes, revert to the yellow colour and shifts its emission to 586 nm (Figure 4). Since the pristine-y form was not stable hence we were not able to get a distinct PXRD pattern for this form and hence the PXRD analysis were carried out for the pristine-o, ground and fumed samples of **PTZTPE-3**. The sharp diffractions for the pristine-o samples of **PTZTPE-3** (Figure S3) suggesting its crystalline nature. The ground sample exhibits extremely weak diffractions but the diffraction peaks are not completely disappeared which reveals loss of crystallinity of pristine-o form on mechanical grinding. The fumed samples however exhibit recovered sharp diffractions thus reveals the restoration of regular crystalline nature. We found that the **PTZTPE-3** can maintain its crystallinity to some extent after being ground. Hence, the PXRD study suggests that the switchable conversion from the one crystalline state to another crystalline powder with low crystallinity should be responsible for the reversible mechanochromism of PTZTPE-3.



**Figure 4** Solid state emission spectra of compounds (a) **PTZTPE-2** and (b) **PTZTPE-3** in pristine, grinded and fumed forms. Photographs (inset) taken under UV illumination. (c) UV and (d) daylight images of pristine-0 and pristine-y forms of **PTZTPE-3** in a single frame.

### Single crystal XRD analysis

To investigate the underlying mechanism for the observed mechanochromic behaviour of **PTZTPE-3**, single crystal XRD analysis were performed (Figure 5 and Figure S4) and the data obtained from X-ray analysis were summarized in Table S2. Our attempt to separate E and Z

isomers of **PTZTPE-3** through recrystallization was not successful. However, during crystallization, we obtained good quality crystal of Z isomer of **PTZTPE-3** which was suitable for X-ray diffraction analysis. The crystal structure of **PTZTPE-3** shows bent shape of phenothiazine and propeller shape of tetraphenylethylene unit (Figure 5(A)). The phenothiazine moiety bends Published on 25 August 2020. Downloaded by Carleton University on 8/25/2020 12:58:11 PM. through S and N atoms with an angle of 139.59° (Figure 5(B)). The phenothiazine moiety shows a dihedral angle of  $52.61^{\circ}$  with phenyl acrylonitrile unit and  $16.04^{\circ}$  with tetraphenylethylene unit (Figure 5(D) and Figure S4(E)), indicating the twisted confirmation of the molecule. The **PTZTPE-3** crystallizes in the triclinic, *P-1* space group. The crystal structure of **PTZTPE-3** shows four intermolecular CH... $\pi$  interactions and one  $\pi$ - $\pi$  interaction with the neighboring molecules. The benzene ring of phenyl acrylonitrile moiety of one PTZTPE-3 molecule interacts with the

The belizene ring of phenyl actylonithe molecy of one **PTZTPE-3** molecule interacts with the two neighboring **PTZTPE-3** molecules through two CH... $\pi$  intermolecular interactions. The one CH... $\pi$  intermolecular interaction was observed with the CH group of tetraphenylethylene moiety of a neighboring **PTZTPE-3** molecule by head to tail arrangement making a linear chain of **PTZTPE-3** molecules as shown by blue dashed lines in Figure S4(A). The second CH... $\pi$  intermolecular interaction was observed with the CH group of phenothiazine moiety of another neighboring **PTZTPE-3** molecule as shown by green dashed lines in Figure S4(B). A slipped  $\pi$ - $\pi$  (4.633 Å) intermolecular interaction was observed between the phenothiazine moiety of one **PTZTPE-3** molecule with the benzene ring of phenyl acrylonitrile moiety of another **PTZTPE-3** molecule (Figure S4(C)). The same phenothiazine moiety also interacts with CH groups of tetraphenylethylene moiety of other neighboring **PTZTPE-3** molecule through two CH... $\pi$  interactions as shown by green dashed lines in Figure S4(D). The crystal packing diagram of **PTZTPE-3** shows a dimeric unit in which the S atom of phenothiazine of one **PTZTPE-3** shows a dimeric unit in which the S atom of phenothiazine of one **PTZTPE-3** shows a dimeric unit in which the S atom of phenothiazine of one **PTZTPE-3** shows a dimeric unit in which the S atom of phenothiazine of one **PTZTPE-3** shows a dimeric unit in which the S atom of phenothiazine of one **PTZTPE-3** shows a dimeric unit in which the S atom of phenothiazine of one **PTZTPE-3** shows a dimeric unit in which the S atom of phenothiazine of one **PTZTPE-3** shows a dimeric unit in which the S atom of phenothiazine of one **PTZTPE-3** shows a dimeric unit in which the S atom of phenothiazine of one **PTZTPE-3** shows a dimeric unit in which the S atom of phenothiazine of one **PTZTPE-3** shows a dimeric unit in which the S atom of phenothiazine of one **PTZTPE-3** shows a dimeric unit in which the S atom of phenothiazine of one **PTZTPE-3** shows a dimeri

molecule interacts with the CN group of a neighboring **PTZTPE-3** molecule through C(9)–N(2)...S(1) interaction (3.327 Å) (Figure 5(C)). The loose molecular packing (CH... $\pi$  intermolecular interactions with lengths of 3.125-3.468 Å) and the slipped  $\pi$ - $\pi$  intermolecular interactions could be the inherent reason for making them readily disorganized by the external stimuli. Hence, are responsible for their mechanochromic behaviour.



**Figure 5** (A) Single crystal structure of **PTZTPE-3** (B) Single crystal structure of **PTZTPE-3** showing bent shape of phenothiazine (C) A dimeric unit of **PTZTPE-3** showing C(9)–N(2)...S(1) interaction (D) Single crystal structure of **PTZTPE-3** showing dihedral angle between phenothiazine and phenyl acrylonitrile moiety.

### Charge-transporting properties, ionization potentials and electron affinities of

### the solid samples.

To estimate potential of compounds **PTZTPE 1–4** as semiconductors for various organic/hybrid electronic applications, charge-transporting properties of thick vacuum-deposited films of **PTZTPE 1–4** with the thicknesses (d) higher than 2  $\mu$ m were studied by the time-of-flight (TOF) experiments recording TOF current transients under positive (for holes) or negative (for electrons) applied external voltages (*V*) using the previously described setups (Figure 6 a,b, S7) <sup>[51]</sup>. Transit

times  $(t_{tr})$  for holes can be well observed from the corresponding TOF transients indicating low dispersity of hole transport. However, transit times for electrons were not observed meaning electron transport was not proved for **PTZTPEs** by TOF measurements. Thus **PTZTPE 1–4** can be considered as hole-transporting compounds. Taking transit times for holes at the different applied voltages, hole mobilities were calculated using the formula  $\mu = d^2 / V t_{tr}$ . Their dependences on electric field are plotted in Figure 6c. Practically the same hole mobilities of  $4.7-7.6\times10^{-6}$ cm<sup>2</sup>/Vs at electric field of 4.6×10<sup>5</sup> V/cm were observed for compounds PTZTPE-2-PTZTPE-4 indicating small effect of electron withdrawing substituents (Table 2). Relatively low hole mobilities may by predictively explained by non-planar molecular structures of PTZTPE-2-**PTZTPE-4** which do not allow their close molecular packing in solid-state as it was discussed in the previous section. Because of slightly different values of field dependence parameter ( $\alpha$ ), their zero-field mobilities were found in relatively large range of  $1.5-43 \times 10^{-9}$  cm<sup>2</sup>/Vs. In contrast, by ca. two orders of magnitude higher hole mobility of  $1.67 \times 10^{-4}$  cm<sup>2</sup>/Vs at the same electric field of  $4.6 \times 10^5$  V/cm was observed for compound **PTZTPE-1**. Such difference can be related to the different molecular packing in solid films of compound PTZTPE-1, and, as a result, more appropriate HOMO-HOMO overlapping for hole hopping between neighboring molecules, in comparison to those of compounds **PTZTPE-2-PTZTPE-4** (Figure S4)<sup>[21]</sup>. Hole-transporting properties of compounds **PTZTPE 1–4** mainly suggest their potential applications as emitters but not as hosts or charge-transporting materials which charge mobility commonly exceeded  $10^{-3}$ cm<sup>2</sup>/Vs<sup>[52]</sup>.



**Figure 6** (a, b) TOF signals for holes for the layers of **PTZTPE-2** and **PTZTPE-3**. (c) Hole mobilities versus electric fields and (d) photoelectron emission spectra of vacuum-deposited films of compounds **PTZTPE 1–4**.

The results of photoelectron emission spectroscopy measurements of solid samples **PTZTPE 1–4** (Figure 6 d, Table 2) show that electron withdrawing substituents expectedly have effect on energy levels of the compounds. The values of ionization potential ( $I_p^{PESA}$ ) of the **PTZTPE-2-PTZTPE-4** having were higher in comparison to that of compound **PTZTPE-1**. It should be noted that values of both  $I_p^{PESA}$  and electron affinity ( $E_a^{film}$ ) for all studied materials are in perfect ranges of 5.48–5.59 and 2.6–3.24 eV for hole and electron injection from electrodes of charge-transporting layers, respectively.

PTZTPE-3	PTZTPE-4					
7.6 × 10 <sup>-6</sup>	4.7 × 10 <sup>-6</sup>					
3.3 × 10 <sup>-9</sup>	4.3 × 10 <sup>-8</sup>					
0.0081	0.0069					
5.56	5.59					
2.32	2.64					
3.24	2.95					
<i>u</i> <sub>h</sub> is hole mobility. <i>µ</i> renkel type mobility p taken for vacuum-dep al band gap taken fro ectron affinity calculat						
unds PTZT	'PE 1–4, va					
exploiting device struct						
n)/TPBi(40	nm)/LiF(0.					
(48 nm)/L	iF(0.5 nm):#					
tting layers of compour						
or hexaaza	triphenylene					

Table 2 Energy levels and hole mobility data for the vacuum-deposited layers of compounds PTZTPE 1-4.

**PTZTPE-2** 

 $6.5 \times 10^{-6}$ 

 $1.5 \times 10^{-9}$ 

0.009

5.63

2.73

2.9

PTZTPE-1

 $1.67 \times 10^{-4}$ 

 $4.2 \times 10^{-6}$ 

0.0055

5.48

2.88

2.6

Compound  $\mu_{\rm h}~({\rm cm}^2\,{\rm V}^{-1}\,{\rm s}^{-1})^*$ 

 $\mu_{\theta}$  (cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>)

 $\alpha \, ({\rm cm} \, {\rm V}^{-1})^{1/2}$ 

I<sub>n</sub><sup>PESA</sup> (eV)

Egfilm (eV)

E<sub>a</sub>film (eV)

\*values recorded at electric field of 4.6×10<sup>5</sup> V/cm.  $\mu_{\rm h}$  is  $u_0$  is zero-field mobility. Field dependence parameter ( $\alpha$ ) of a Poole–Frenk redicted by the relationship  $\mu = \mu_0 e^{\alpha E^{1/2}}$ . I<sub>p</sub><sup>PESA</sup> is ionization potential take osited films by photoelectron spectroscopy in air (PESA), Eg is optical b om low-energy onsets of absorption spectra in solid state,  $E_a{}^{\rm film}$  is electro ted by formula  $E_a^{\text{film}} = I_p - E_g^{\text{film}}.$ 

### **Electroluminescent properties.**

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Aiming to study electroluminescent properties of compounds cuum-deposited and solution-processed non-doped OLEDs were fabricated expl tures ITO/HAT-CN(8 nm)/TCTA(32 nm)/EML (24 nm)/TSPO1(8 nm)/TI 5 nm):Al and ITO/HAT-CN (8 nm)/EML (40 nm)/TSPO1 (8 nm)/TPBi (48 Al, respectively. The EML were vacuum-deposited or spin-coated light-emitting nds PTZTPE-1, PTZTPE-2, PTZTPE-3 or PTZTPE-4. Hole-injector h ehexacabonitrile tris(4-carbazoyl-9-ylphenyl)amine (TCTA), (HAT-CN), hole-transporter hole-blocker diphenyl[4-(triphenylsilyl)phenyl]phosphine oxide (TSPO1); electron-transporter 2,2',2''-(1,3,5benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi), electron-injector fluorolithium (LiF) were

selected for the vacuum-deposited devices. The hole-transporting layer of TCTA was not used in solution-processed OLEDs to prevent its washing-out during spin-coating of EML of emitters of **PTZTPE** family. The relationship between energy levels of the selected functional materials are demonstrated in Figure 7 a. According this relationship, good hole/electron injection to the lightemitting layers and hole/electron blocking within these layers is expected. This expectation is in very good agreement with the electroluminescence (EL) spectra of non-doped devices which were completely related to emission of **PTZTPE** emitters (Figure 7). The similar EL spectra were recorded at different voltages meaning that hole-electron recombination zone was not shifted to the hole or electron transporting layers (Figure S8). The CIE colour coordinates of the vacuumprocessed non-doped OLEDs were related to greenish-blue for device based on PTZTPE-2, green for device based on **PTZTPE-1**, yellowish-green for device based on **PTZTPE-4**, and orange for device based on PTZTPE-3 (Figure S9, Table 3). Interestingly, PTZTPE-1-based vacuumprocessed OLEDs and PTZTPE-4-based solution-processed OLEDs showed EL spectra with two bands. This observation is apparently related to MCL properties of the compounds when two kind of aggregates are formed under the vacuum deposition/solution processing<sup>[21]</sup>. There are evidences in the literature that different electroluminescence spectra can be obtained using the same emitter with mechanofluorochromic properties <sup>[53-55]</sup>. Such electroluminescence colour changes were obtained due to treatments of light-emitting layers of MCL emitter-based OLEDs. Different electroluminescence spectra can be obtained when the light-emitting layer will be spin coated using different solvents for spin coating of MCL emitter <sup>[56]</sup>. Such result was explained by formation of different conformers of the same MCL molecule depending on the fabrication technology of light-emitting layers. Apparently, different deposition methods (solution or vacuumprocessed ones) caused formation of different ratio of either MCL forms or molecular conformers

in the light-emitting layers resulting in different EL spectra of **PTZTPE-1** and **PTZTPE-4** nondoped OLEDs under electrical excitation. Such effect is more evident for compounds **PTZTPE-1** and **PTZTPE-4** since their MCL forms were characterized by more different emission spectra that those of compounds **PTZTPE-2** and **PTZTPE-3**.



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**Figure 7** (a) Energy levels of the functional layers of non-doped (fluorescent) and doped (hyperelectrofluorescence based) devices. The energies are given in eV. The figure includes chemical structure of the conventional blue fluorescent polymeric emitter TFB and TADF co-host pCNBCzoCF<sub>3</sub>. (b) EL spectra at 6V of vacuum-processed and solution-processed non-doped OLEDs based on the corresponding **PTZTPE** emitters and PL spectra of their neat layers.

Maximum EQE values of vacuum-processed OLEDs were found in the range 1.03–1.73% (Table 3). This result is in good agreement with PLQY values of the corresponding light-emitting layers (24% for **PTZTPE-1**, 28% for **PTZTPE-2** and for **PTZTPE-3**, 19% for **PTZTPE-4**) taking into account a formula  $\eta_{ext}=\gamma \times PLQY \times \chi \times \eta_{out}$  (Formula 1) where the charge balance factor  $\gamma$  is of 1 for the perfectly optimized device structure, the efficiency of exciton production  $\chi$  is of 0.25 for conventional fluorescent emitters such as **PTZTPEs**, the outcoupling efficiency  $\eta_{out}$  is of 0.2-0.3 for glass subtract based devices <sup>[23]</sup>. Maximum EQE values of solution-processed OLEDs were

found to be considerably lower apparently because of the absence of hole-transporting layers in their structures leading to decrease of the charge balance factor  $\gamma$ . Very low maximum EQE of 0.027% was obtained for solution-processed **PTZTPE-4**-based OLEDs in contrast to that of vacuum-deposited ones. This result is related to the quality of spin-coated films based on compound **PTZTPE-4**. Similarly, efficiency of **PTZTPE-4**:pCNBCzoCF<sub>3</sub>:mCP-based device was much lower than efficiencies of **PTZTPE-1**:pCNBCzoCF<sub>3</sub>:mCP-based and **PTZTPE-3**:pCNBCzoCF<sub>3</sub>:mCP-based analogs (Table 3).

PLQY values of 3, 30, 66, and 6% were obtained for low-polarity toluene solutions of PTZTPE-1, PTZTPE-2, PTZTPE-3 and PTZTPE-4, respectively. Taking into account PLQYs of the corresponding solutions, the usage of appropriate hosts can predictively allow to enhance PLQYs values in solid state at least for compounds PTZTPE-2 and PTZTPE-3. Indeed, PLQY values of 30, 24, 39, and 17% were obtained for mCP-doped films of PTZTPE-1, PTZTPE-2, PTZTPE-3 and **PTZTPE-4**, respectively. However, these values may allow only slightly to increase the EQEs of the **PTZTPEs**-based devices. To improve the efficiency of exciton production from  $\gamma=0.25$  to  $\gamma = 1$  in the **PTZTPEs**-based OLEDs, TADF exhibiting compound pCNBCzoCF<sub>3</sub> was selected as co-host (Figure 7a) <sup>[41,42]</sup>. pCNBCzoCF<sub>3</sub> was selected taking into account to the requirements for hyperfluorescence discussed in the introduction. For example, HOMO<sub>PTZTPE-3</sub>> HOMO<sub>pCNBCzoCF3</sub>>HOMO<sub>mCP</sub> and LUMO<sub>PTZTPE-3</sub><LUMO<sub>pCNBCzoCF3</sub><LUMO<sub>mCP</sub> (Figure 7a). The different absorption-emission spectral overlaps of co-hosts:emitter systems was identified for compounds PTZTPE-3 and PTZTPE-2 (Figure S10a). PL spectra of non-doped films of **PTZTPE-1**, **PTZTPE-3** and **PTZTPE-4** were red-shifted in comparison to PL spectrum of the non-doped film of pCNBCzoCF<sub>3</sub> supposing efficient co-host $\rightarrow$ emitter FRET (Figure S10b). In contrast, PL spectrum of film PTZTPE-2 is blue-shifted comparing to that of the film of

pCNBCzoCF<sub>3</sub> supposing inefficient FRET from pCNBCzoCF<sub>3</sub> to **PTZTPE-2**. In addition, it is

not possible to get white electroluminescence mixing the blue emissions of TFB and PTZTPE-2. Therefore, compound PTZTPE-2 was not used for the development of pCNBCzoCF3-based hyperfluorescence systems. The doped films of the systems PTZTPE-1:pCNBCzoCF<sub>3</sub>:mCP, **PTZTPE-3**:pCNBCzoCF<sub>3</sub>:mCP and **PTZTPE-4**:pCNBCzoCF<sub>3</sub>:mCP with hyperfluorescence properties were prepared by spin coating with the optimized concentrations of 2, 15 and 83 wt% of **PTZTPEs**, pCNBCzoCF<sub>3</sub> and mCP respectively. To develop white hyperelectrofluorescent OLEDs, the solution-processing was selected mainly because of the possibility to better control the doping concentration in comparison to vacuum based one. It is important especially in our case when the three component- based light-emitting layer PTZTPE-3(2 wt%):pCNBCzoCF<sub>3</sub>(15 wt%):mCP(83 wt%) with precisely optimized concentration was used in the device structure. Moreover, there is practical interest for solution-processing technology since it is appropriate for large area devices and it has its own advantages (e.g., high processing efficiency, low-cost, lowwaste of materials, easy scalability) in comparison to the vacuum technology <sup>[57]</sup>. PL spectra of the PTZTPE-1:pCNBCzoCF<sub>3</sub>:mCP, films of co-host containing **PTZTPE**systems **3**:pCNBCzoCF<sub>3</sub>:mCP and **PTZTPE-4**:pCNBCzoCF<sub>3</sub>:mCP were completely related to emission of compounds PTZTPE-1, PTZTPE-3 or PTZTPE-4 proving perfect energy transfer from hosts to the emitter of low concentration (2%), (Figure 8a). Meanwhile, PL decays of co-host-based films were characterized by longer lifetimes in comparison to the prompt fluorescence lifetimes of **PTZTPEs (Figure 8b, Table S6)**. This observation may be explained by triplet harvesting via TADF host pCNBCzoCF<sub>3</sub> which typically is attributed to hyperfluorescence  $^{[30-32]}$ . PL decay of the system **PTZTPE-3**:pCNBCzoCF<sub>3</sub>:mCP was fitted by single exponential function with the lifetime of 6.7 ns due to the efficient FRET. The systems PTZTPE-1:pCNBCzoCF<sub>3</sub>:mCP and

**PTZTPE-4**:pCNBCzoCF<sub>3</sub>:mCP systems were characterized by double exponentials PL decays (**Figure 8b, Table S6**). The efficient FRET of the system **PTZTPE-3**:pCNBCzoCF<sub>3</sub>:mCP can be explained big absorption-emission spectral overlap with the emission-absorption of pCNBCzoCF<sub>3</sub> (Figure S10). Hyperfluorescence allows to obtain the efficiency of exciton production with theoretical limit of 100% under electrical excitation<sup>[29-31]</sup>. Predictively, EQEs of **PTZTPEs**-based OLEDs can be significantly improved according to their hyperfluorescence with  $\chi$  of 1 (**Figure 8, Formula 1**).



**Figure 8.** PL spectra (a) and PL decay curves (b) of the doped spin-coated films co-host:host (pCNBCzoCF<sub>3</sub>:mCP), emitter:host (**PTZTPEs:**mCP) and emitter:co-host:host (**PTZTPEs:**pCNBCzoCF<sub>3</sub>).

Mixing orange hyperfluorescence of the system **PTZTPE-3**:pCNBCzoCF<sub>3</sub>:mCP with blue emission of the layer of polymer TFB <sup>[58]</sup> (Figure 9a, S10), it is predictively possible to obtain white hyperelectroluminescence similar to that of many other types of white OLEDs (Figure 9a) <sup>[59-61]</sup>. The corresponding coordinates can be found in Figure 9a. If to draw a line through those CIE colour coordinates of **PTZTPE-3**:pCNBCzoCF<sub>3</sub>:mCP and TFB, this line will go near the coordinate of nature white (0.33, 0.33). This analyse means that white electroluminescence can be

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obtained by mixing emission of TFB and PTZTPE-3 if the device structure is well optimized. To this prediction. **OLEDs** with the prove structure ITO/MoO<sub>3</sub>(2nm)/TFB(40nm)/EML(40nm)/TSPO1(8nm)/TPBi(40)/LiF:A1 were fabricated using the systems PTZTPE-1:pCNBCzoCF<sub>3</sub>:mCP, PTZTPE-3:pCNBCzoCF<sub>3</sub>:mCP or PTZTPE-4:pCNBCzoCF<sub>3</sub>:mCP as EML. Step-by-step spin-coating of the TFB and EML layers was possible since the layer TFB was insoluble after its thermal treatment at 150 °C during 30 min in nitrogen atmosphere. In solution-processed OLEDs, the layer of TFB acted not only as blue emitter but also as hole-transporting and electron-blocking layer due to its high hole mobility (ca.  $2 \times 10^{-3}$  cm<sup>2</sup>/Vs at the electric field of  $2.5 \times 10^5$  V/cm), low ionization potential (5.3 eV) and high electron affinity (2.3 eV) <sup>[62]</sup>. Because of both good balance of hole and electron mobilities within EML and hyperelectroluminescence phenomenon, maximum EQEs of solution processed OLEDs based on the systems **PTZTPE-1**:pCNBCzoCF<sub>3</sub>:mCP, **PTZTPE-3**:pCNBCzoCF<sub>3</sub>:mCP or **PTZTPE-**4:pCNBCzoCF<sub>3</sub>:mCP were much improved in comparison to EQEs of non-doped PTZTPEsbased solution processed devices (Figure 9b, Table 3). EQE of 8.2% was obtained for OLED based on the system PTZTPE-3:pCNBCzoCF<sub>3</sub>:mCP. The low turn-on voltage of 4.5 V and the high maximum brightness of 3400  $cd/m^2$  were recorded for the device (Figure 9c, Table 3). Electroluminescence of TADF and/or phosphorescent (rare-earth-atom-containing) emitters is mainly exploited in state-of-art white OLEDs <sup>[63, 64]</sup>. Meanwhile, examples of efficient white electroluminescence from simple fluorescent emitters only (from hyperfluorescence only, thus without TADF or phosphorescence) are very limited due to the best of our knowledge. Those examples are related to vacuum-deposited white OLEDs with maximum EQE of 12.1 and 12.9% in the best cases [46, 47]. EQE (8.2 %) of the developed white solution-processed PTZTPE-3-based

hyperelectrofluorescence-based OLEDs is not far below of the efficiencies of the mentioned examples.



**Figure 9** CIE1931 colour coordinates (a) for blue and orange emissions of spin-coated lightemitting layers of TFB and **PTZTPE-3**: pCNBCzoCF<sub>3</sub>:mCP as well as for EL spectra recorded at different voltages (the step is 1V) of OLEDs based on those layers. The inset shows CRI-applied voltage dependence of OLEDs. EQE-current density (b) voltage-current density and voltagebrightness (c) characteristics as well as EL spectra at different applied voltages of the solution processed hyperelectroluminescence based devices.

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OLEDs based on the system **PTZTPE-3**:pCNBCzoCF<sub>3</sub>:mCP were characterized by EL spectra with CIE1931 colour coordinates ((0.28, 0.38) at 6V) close to the CIE colour coordinates (0.33, 0.33) of nature white (Figure 9a,d, Table 3). White hyperelectroluminescence with CRI value of 67 at 6 V was obtained for such OLEDs (Figure 9a, inset, Table 3). In the well-optimized device structure, such result can be explained by overlapping of blue emission of TFB and orange emission of PTZTPE-3 of the similar intensities. It should be noted that PL spectrum of pCNBCzoCF3:mCP film shows a peak of ~440 nm (Figure 8a). The EL spectra of PTZTPE-3based OLEDs are characterized by the high-energy band peaked at wavelength of ~440 nm (Figure 9d). Despite similar maximum wavelengths (~440 nm) of PL spectrum of pCNBCzoCF3: mCP film and EL spectra of PTZTPE-based OLEDs, the observed bands are originated from different emitters from pCNBCzoCF3 (in case of PL spectrum of the pCNBCzoCF3:mCP film) and from TFB (in case of **PTZTPE-3**-based OLEDs). Mainly, it is explained by the fact that there is no pCNBCzoCF3:mCP film in the studied device structure. In the device structure, there is three component-based film PTZTPE-3:pCNBCzoCF3:mCP which emission is resulted from the emitter PTZTPE-3 but not from pCNBCzoCF3 (Figure 8a). It is also evident from comparison of EL spectra of the studied devices with PL spectrum of TFB and pCNBCzoCF3:mCP films since 1) the shape of the blue band of EL spectra is very similar to the shape of PL spectrum of TFB film but not to that of pCNBCzoCF3:mCP film; and 2) the set-on of PL spectrum of pCNBCzoCF3:mCP film and EL spectra of PTZTPE-based devices as well as the set-on of PL spectrum of TFB film are at different wavelengths (Figure S10c).

Because of electron-blocking properties of TFB layer and hole blocking properties of TSPO1 layer (Figure 7a), the injected hole-electron pairs recombine within the orange light-emitting layer on mCP and pCNBCzoCF<sub>3</sub> co-hosts forming both singlet and triplet excitons. Triplets can be

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converted to singlets due to RISC of TADF co-host pCNBCzoCF<sub>3</sub>. At the same time, singlets can be transferred from co-host mCP to blue TFB emitter and from co-host pCNBCzoCF<sub>3</sub> to orange emitter **PTZTPE-3** via FRET mechanism (Figure 1b, 7a). Stable color of white hyperelectroluminescence is expected in such case. However, intensity of blue band of EL spectra of OLEDs based on the system **PTZTPE-3**:pCNBCzoCF<sub>3</sub>:mCP-based OLEDs increased with increasing of applied voltages (Figure 9d). This observation can apparently be attributed to direct hole-electron recombination within TFB layer which lead to slight instability of white color of the devices based on the system **PTZTPE-3**:pCNBCzoCF<sub>3</sub>:mCP (Figure 7a). More stable colors of obtained for OLEDs based on electroluminescence were the systems PTZTPE-1:pCNBCzoCF<sub>3</sub>:mCP and PTZTPE-4:pCNBCzoCF<sub>3</sub>:mCP (Figure 9d). However, their EL spectra were far from white since emission spectra of PTZTPE-1 and PTZTPE-4 in the co-hosted films were close to emission spectrum of the layer of TFB.

### Table 3. Output parameters of the PTZTPEs-based OLEDs.

EMI	Brightness	External quantum	CIE*	CDI*				
ENIL	$(cd/m^2)$	efficiency, (%)	(x, y)	CRI*				
Vacuum-deposited non-doped OLEDs: ITO/HAT-CN/TCTA/EML/TSPO1/TPBi(40 nm)/LiF:Al								
PTZTPE-1	8055	1.07	(0.17, 0.44)	-				
PTZTPE-2	3600	1.53	(0.54, 0.46)	-				
PTZTPE-3	3916	1.03	(0.28, 0.47)	-				
PTZTPE-4	470	1.73	(0.32, 0.55)	-				
Solution-processed non-doped OLEDs: ITO/HAT-CN/EML/TSPO1/TPBi(40 nm)/LiF:Al								
PTZTPE-1	2150	0.68	(0.16, 0.48)	-				
PTZTPE-2	2720	0.29	(0.57, 0.44)	-				
PTZTPE-3	2235	0.28	(0.27, 0.49)	-				
PTZTPE-4	430	0.027	(0.35, 0.57)	-				
Solution-processed doped OLEDs: ITO/MoO <sub>3</sub> /TFB/EML/TSPO1/TPBi/LiF:Al								
PTZTPE-1: pCNBCzoCF <sub>3</sub> :mCP	940	3.9	(016 0 10)	_				
(2:15:83wt%)	510		()					
PTZTPE-3: pCNBCzoCF <sub>3</sub> :mCP	3400	8.2	(0.28, 0.38)	67				
(2:15:83wt%)	5100		(0.20, 0.30)	07				
PTZTPE-4: pCNBCzoCF <sub>3</sub> :mCP	2200	0.7	(0.17, 0.21)					
(2:15:83wt%)	00		(0.17, 0.21)					

\*CIE and CRI data are given for EL spectra at 6V.

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### Conclusion

Design strategy of mechanochromic triads containing phenothiazine, tetraphenylethylene and electron withdrawing groups which allowed to achieve combination of the properties required for white hyperelectroluminescence. Optical properties of the synthesized phenothiazine based tetraphenylethylene derivatives were found to be greatly dependent on the nature of electron withdrawing substituents. The **PTZTPE-2** and **PTZTPE-3** showed substituent dependent unique stimuli responsive luminescence characteristics. On grinding, the **PTZTPE-2** hypsochromically shifts its emission to shorter wavelength whereas, the **PTZTPE-3** exhibits "back and forth" type switching in its emission in response to mechanical grinding. One derivative of phenothiazine and tetraphenylethylene showed promising performance in white hyperfluorescence. It was used for development of solution-processed OLED with two light-emitting layers. The device exhibited white hyperelectrofluorescence with CRI of 67, color coordinates of (0.28, 0.38) and maximum external quantum efficiency of 8.2%. The proposed approach for white hyperelectrofluorescence may be used not only for solution-processable but also for vacuum-processable OLEDs. It is believable that further usage of efficient fluorescent emitters will give rise in efficiency of white hyperelectrofluorescence based simply produced OLEDs.

### **Experimental section**

### **General methods**

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under a nitrogen/argon atmosphere. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded on a Bruker 400 MHz FT-NMR spectrometer at room temperature. <sup>1</sup>H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent

residual peak (CDCl<sub>3</sub>, 7.26 ppm). Multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet) and the coupling constants, *J*, are given in hertz. <sup>13</sup>C NMR chemical shifts are reported relative to the solvent residual peak (CDCl<sub>3</sub>, 77.0 ppm). UV-visible absorption spectra were recorded on a PerkinElmer Lambda 35 instrument. Emission spectra were taken in a Fluoromax-4C, S/n.1579D-1417- FM Fluorescence software Ver 3.8.0.60. The relative quantum yields in solution were calculated using Quinine sulphate in 0.5 M H<sub>2</sub>SO<sub>4</sub> as standard for **PTZTPE-2** and rhodamine-6G as standard in ethanol for **PTZTPE-3**. All the measurements were carried out at 25 °C. HRMS was recorded with a Bruker-Daltonics micrOTOF-Q II mass spectrometer. Single-crystal X-ray structural studies of **PTZTPE-3** was performed on a CCD equipped SUPERNOVA diffractometer from Agilent Technologies with Oxford Instruments low-temperature attachment under argon/nitrogen using standard Schlenk and vacuum-line techniques.

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Synthesis of PTZTPE-2 : A mixture of TPE-Bpin (0.4 g, 0.87 mmol), 7-bromo-10-propyl-10Hphenothiazine-3-carbonitrile (5) (0.36 g, 1.05 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.055 g, 0.05 mmol) and potassium carbonate (0.360 g, 2.61 mmol) were dissolved in THF/ethanol/water (9/3/1 v/v/v) and purged for 10 minutes. After, heated to reflux for 14 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into water. The organic layer was extracted with dichloromethane and the combined organic layers were washed with saturated brine solution and water and dried over anhydrous sodium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane (2/3 v/v) as eluent. Light green solid of **PTZTPE-2** was obtained in 78% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40 (d, *J* = 8.5 Hz, 1H), 7.34 (d, *J* = 9.4 Hz, 2H), 7.27 (s, 2H), 7.25 (s, 1H), 7.14 – 7.02 (m, 17H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 3.83 (t, *J* = 7.0 Hz, 2H), 1.88 – 1.78 (m, 2H), 1.02 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.14, 143.80, 142.99, 142.56,

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141.36, 140.52, 137.23, 136.40, 131.90, 131.48, 130.48, 128.18, 127.58, 126.61, 126.16, 125.75, 125.45, 123.85, 118.97, 116.21, 115.14, 105.22, 49.66, 20.07, 11.31 ppm. HRMS (ESI): Calcd. for C<sub>42</sub>H<sub>32</sub>N<sub>2</sub>S [M]<sup>+</sup>: 596.2281, Found: 596.2280.

Synthesis of PTZTPE-3 : A mixture of TPE-Bpin (0.4 g, 0.87 mmol), (Z)-3-(7-bromo-10propyl-10H-phenothiazin-3-yl)-2-phenylacrylonitrile (6) (0.47 g, 1.05 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.055 g, 0.05 mmol) and potassium carbonate (0.360 g, 2.61 mmol) were dissolved in THF/ethanol/water (9/3/1 v/v/v) and purged for 10 minutes. After, heated to reflux for 14 h under nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into water. The organic layer was extracted with dichloromethane and the combined organic layers were washed with saturated brine solution and water and dried over anhydrous sodium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using hexane/dichloromethane (2/3 v/v) as eluent. An orange solid of **PTZTPE-3** was obtained in 69% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.73 (d, J = 8.5 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.45 (s, 1H), 7.34 (d, J = 7.4 Hz, 1H), 7.30 (t, J = 6.0 Hz, 2H), 7.23 (d, J = 10.3 Hz, 1H), 7.19 (s, 1H), 7.15 (m, 2H), 6.99 (m, 18H), 6.87 - 6.45 (m, 3H), 3.71 (m, 2H), 1.76 (m, 2H), 0.95 (t, J = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.96, 143.86, 143.04, 142.77, 141.26, 140.90, 140.61, 137.48, 135.73, 134.88, 131.95, 131.50, 129.65, 128.93, 128.78, 127.90, 126.59, 126.08, 125.23, 124.48, 124.14, 118.57, 115.79, 115.20, 108.75, 49.62, 20.15, 11.36 ppm. . HRMS (ESI): Calcd. for C<sub>50</sub>H<sub>38</sub>N<sub>2</sub>S [M]<sup>+</sup>: 698.2750, Found: 698.2750.

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