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# Reversibly Switchable Phase-Dependent Emission of Quinoline and Phenothiazine Derivatives Towards Applications in Optical Sensing and Information Multi-Coding

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Abstract: Three new quinoline and di-tert-butyl phenothiazine isomeric derivatives were synthesized and characterized towards applications for oxygen sensing and optical information multi-coding. The compounds with phenylene linker showed outstanding phasedependent reversibility between ON/OFF stages (low and high emission intensity, drastic shifting of emission colors, short- and longlived fluorescence) under systematic grinding-fuming cycles required for multichannel memory devices based on optical information multicoding. The conformational diversity of phenothiazine unit endowed dual emission of the doped films implemented by the different luminescent mechanisms with peaks located at 414/530 nm, 416/540 nm and 440/582 nm. The presence of phenylene linker and thus two rotational degrees of freedom resulted in quenching of delayed fluorescence of quasi-equatorial conformers in the solid state. The compound containing no phenylene bridge was characterized by two different driving photoluminescence mechanisms of the doped films: short fluorescence of quasi-axial conformer and TADF of quasiequatorial form. This compound showed oxygen sensitivity with the Stern–Volmer constant of 7.5.10<sup>-4</sup> pmm<sup>-1</sup>.

#### Introduction

Aromatic, π-conjugated organic compounds with donor-acceptor framework are an object of intensive scientific interest during last decades because of their effective utilization in the field of organic electronics. Such compounds found application as hosts for OLEDs,<sup>[1,2]</sup> emitters in heavy-metal-free OLEDs,<sup>[3,4]</sup> absorbing materials in dye-sensitized solar cells,<sup>[5]</sup> and as hole-transporting materials showing not only efficient TADF, but aggregation induced emission, polymorphism or mechanoluminescence are of great demand affording new design strategies <sup>[7–9]</sup> and applications in non-doped OLEDs. <sup>[10,11]</sup> Since the first report in 2013,<sup>[12]</sup> TADF emitters were characterized as effective radiometric sensors of oxygen.<sup>[13]</sup> Luminescent materials with the ability to alternate emission wavelength under mechanical stimuli,

hold an important place in organic electronics due to their applications in memory storage, mechanosensors and secure inks.<sup>[14,15]</sup> Moreover, materials exhibiting mechanically included delayed fluorescence are of great interest as they can be applied in oxygen and flexible pressure sensors,<sup>[16]</sup> for luminescence biological imaging<sup>[17]</sup> and data storage. To the best of our knowledge, there are only few reports on mechanoluminescent (ML) materials with mechanically stimulated TADF and "turnon/off TADF".[18-20] Materials exhibiting on/off transitions of emission are potential candidates for memory devices (data storage) with multi-coding properties (Figure 1a). Three channels of coding/decoding of optical information can be realized using the synthesized compounds. Channel 1: Coding/decoding by emission intensity. The differences of 2-3 times in emission intensities were observed for ON/OFF stages ("0"/"1" coding/recoding). Channel 2: Coding/decoding by emission wavelengths. The emission colors of the compounds were reversibly switchable from blue/green (478/506 nm) of asprepared crystalline solids (stage OFF) towards yellow after mechanical grinding (538/564 nm) and melting (540/569 nm) (stage ON). Channel 3: TADF with long-living component (1.5-1.9 µs) of the compounds with phenyl linker was rapidly switched on/off.





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Data encryption realized by the hardware encoding devices is probably the most prominent and essential application of such kind of materials with several condition-switching properties. There are examples of application of inorganic-organic composites for the multi-coding purposes.<sup>[21]</sup> However purely organic materials also may be applied successfully in the similar devices.<sup>[22]</sup> They assure specific advantages, such as tunability, flexibility etc.

In our study, we report on materials with reversibly switchable emission, different in color, intensity and PL lifetimes towards optical sensing and information multi-coding for memory devices (Figure 1b). With this propose, derivatives of phenothiazine and quinoline with donor-acceptor (D-A) and donor- $\pi$ -acceptor (D- $\pi$ -A) structures were synthesized and characterized. D-A type compound (3,7-di-*tert*-butyl-10-(2,4-diphenylquinolin-6-yl)-10H-phenothiazine (PZPQ) showing ML/constant TADF was applied for the fabrication of oxygen sensing devices.

D- $\pi$ -A type compounds (3,7-di-*tert*- butyl-10-(4-(4-phenylquinolin-2-yl)phenyl)-10*H*-phenothiazine (pPZPQ) and 3,7-di-*tert*-butyl-10-(3-(4-phenylquinolin-2-yl)phenyl)-10*H*-phenothiazine

(mPZPQ) (Figure 1b) demonstrated ML and switchable TADF. Although, ML and constant TADF were previously shown for the phenothiazine derivatives,<sup>[23,24]</sup> the ability of two presented here compounds, mPZPQ and pPZPQ (Figure 1b) to show reversibly switchable emission from purely singlet emission to TADF under mechanical stimuli is a unique property which potentially can find application in memory devices. This assumption is supported by reversibility/stability tests showing stable transition between singlet emission and TADF which can be systematically repeated over several grinding-fuming cycles.

#### **Results and Discussion**

#### Synthesis and characterization

The synthesis of target compounds is depicted in Scheme 1. Synthetic pathways towards quinoline-based compounds were similar to the previously reported ones.<sup>[25]</sup> The first step was acidcatalyzed Friedlander cyclocondensation to yield a halogenated quinoline derivative. This reaction was followed by the BuchwaldHartwig cross-coupling reaction of halide-containing quinoline derivative and di-*tert*-butyl-phenothiazine NH-donor to gain the target compounds. The chemical structures of pPZPQ, mPZPQ and PZPQ were proved by <sup>1</sup>H and <sup>13</sup>C NMR, mass spectrometries and elemental analysis (see experimental section in SI).



Scheme 1. Synthetic routes towards compounds pPZPQ, mPZPQ and PZPQ.

#### Thermal, electrochemical and photoelectrical properties

The thermal properties of the synthesized materials were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere. The results are shown in Figure 2. Thermal characteristics are summarized in Table 1. The 5%-weight loss temperatures were found to be close for all three compounds and were situated in the range of 348–385 °C. The highest 5% weight loss temperature was observed for pPZPQ. It was by 25 °C higher than that of *meta*- isomer. This difference can be attributed to the stronger intermolecular interactions of pPZPQ, caused by denser packing of pPZPQ molecules which is possible due to more symmetrical structure of *para*-isomer.<sup>[26]</sup>



Figure 2. (a) TGA curves, (b) cyclic voltammograms and (c) photoelectron emission spectra of pPZPQ, mPZPQ and PZPQ.

In TGA experiments complete weigh loss was observed for the samples of mPZPQ and PZPQ, which is the evidence of sublimation process (Figure 2a). The target compounds were obtained after the synthesis and purification as crystalline substances. Therefore, they showed endothermic melting signals during the first DSC heating scans (Figure S1). Compound pPZPQ exhibited slightly higher melting temperature of 244 °C in comparison with that of the corresponding *meta*-isomer mPZPQ which melted at 230 °C. This observation again can be explained by the stronger intermolecular interaction in the crystals of *para*-isomer. All three compounds were capable to form molecular architectures, compounds exhibited close glass transition temperature values, which were in the range of 114–116 °C.

Table	1.	Thermal	and	electrochemical	properties	of	pPZPQ,	mPZPQ	and
PZPQ.									

Compound	E <sub>ox</sub> <sup>[a]</sup> V	E <sub>red</sub> <sup>[a]</sup> V	IP <sub>CV</sub> <sup>[b]</sup> eV	EA <sub>CV</sub> <sup>[b]</sup> eV	IP <sub>PE</sub> <sup>[c]</sup> eV	T <sub>d-5%,</sub> <sup>[d]</sup> °C	Tg <sup>[e]</sup> °C	T <sub>m</sub> [e] °C
pPZPQ	0.31	-1.95	5.11	2.85	5.43	385	115	244
mPZPQ	0.35	-1.95	5.15	2.85	5.40	360	116	230
PZPQ	0.26	-1.98	5.06	2.82	5.33	348	114	243

[a] Estimated from CV data; [b] Estimated using the approximation  $IP_{CV} = |e|(4.8 + E_{ox}); EA_{CV} = |e|(4.8 + E_{red}); [c] Estimated from photoelectron emission spectra; Estimated from [d] TGA and [e] DSC.$ 

Cyclic voltammetry (CV) was employed for the estimation of ionization potentials (IP<sub>CV</sub>) and electron affinities (EA<sub>CV</sub>) of the compounds. CV curves are shown in Figure 2b. The respective electrochemical data are collected in Table 1. Due to the similar structure of the compounds, which contain electron-rich 3,7-ditert-butyl phenothiazine heterocycle and electron-deficient phenyl-quinolin-yl aromatic system, their CV curves were found to have analogous shapes. The compounds demonstrated both reversible oxidation and reduction processes during the first CV scans. Oxidation potential values were found to be 0.31 V for pPZPQ, 0.35 V for mPZPQ and 0.26 V for PZPQ, while reduction potentials were found to be -1.95 for pPZPQ and mPZPQ and -1.98 for PZPQ. The IP<sub>CV</sub> and EA<sub>CV</sub> values were calculated using the equations:  $IP_{CV} = |e|(4.8 + E^{ox}_{onset}); EA_{CV} = |e|(4.8 + E^{red}_{onset}).$ The obtained values of  $IP_{CV}$  and  $EA_{CV}$  are given in Table 1. Considering minor differences in the structure of the compounds, the IP<sub>CV</sub> and EA<sub>CV</sub> values were found to be expectedly close. The lowest IP<sub>CV</sub> value of 5.06 eV was demonstrated by PZPQ and can be assigned to the direct, spacerless D-A linkage.<sup>[27]</sup> Ionization potentials of the materials were also estimated for the solid samples with utilization of photoelectron emission spectrometry (Figure 2c). The obtained IP<sub>PE</sub> values were found to be higher than the corresponding IP<sub>CV</sub> values, which is common observation, and apparently is related to the presence of intermolecular interactions (e. g.  $\pi$ - $\pi$  stacking) in the solid state. The IP<sub>PE</sub> values obtained by photoelectron emission spectrometry varied from 5.33 to 5.44 eV (Table 1).

To demonstrate the potential of compounds pPZPQ, mPZPQ and PZPQ as light-emitting materials, charge-transporting properties of their vacuum deposited layers were investigated by time of flight (TOF) technique. Bipolar charge transport with relatively

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strong dispersity was observed for all the compounds (Figure S2). Electron and hole mobilities exceeded  $10^{-4}$  cm<sup>2</sup>/Vs in the layers of compound pPZPQ at electric fields higher than  $3 \times 10^5$  V/cm (Figure S2). Considerably lower electron and hole mobilities were detected for the layers of compounds mPZPQ and PZPQ at the same electric fields. Superior charge-transporting properties of pPZPQ are presumably related to the favorable molecular packing with high number of close CH···π interaction sites in solid state. For compounds mPZPQ and PZPQ, such interactions are limited. The synthesized compounds are promising candidates for the applications in organic optoelectronic devices due to their balanced charge-transporting properties and abilities of triplet harvesting.

#### **Theoretical studies**

To get deeper insight into the conformational diversity<sup>[28]</sup> of the structures of pPZPQ, mPZPQ and PZPQ, optimization of ground state geometries of quasi-axial (g-ax) and guasi-equatorial (g-eg) phenothiazine conformers was performed using B3LYP/6-31G (d. p) basis set in vacuum. Also, comparative stability and possibility of existence of different molecular conformations were estimated by comparison of energies of the ground state of the conformers (Table S1). For all the molecules, g-ax forms were found to be slightly more stable in comparison to the q-eq conformers (their theoretical energies of the ground state are lower by ca. 1.5 kcal/mol). Minor energy differences of two conformers for each compound suggest that both species with the different excited states can exist. The time-dependent density functional theory method (TD-DFT) with the 6-31G (d, p) basis set was used to understand the nature of excited states of q-ax and q-eq conformers of the compounds. The optimized geometries of the ground and excited states (S1, T1) of the compounds with the different phenothiazine conformers are depicted in Figure 3. In the ground state q-ax conformers of compounds pPZPQ, mPZPQ and PZPQ adopted more planar conformations with dihedral angles between di-tert-butyl phenothiazine and phenylquinoline units of 8°, 4° and 5°, respectively. Meanwhile, q-eq conformers of pPZPQ, mPZPQ and PZPQ showed dihedral angles of 81°, 81°, and 80° respectively (Figure 3).

To investigate the electronic transitions, theoretical UV-vis spectra were obtained for each conformer with up to 40 calculated excited states. For better visualization, experimental UV-vis spectra of THF solutions are shown along with the theoretical absorption spectra of the compounds in Figure S3. Experimental spectra are in good agreement with the theoretical ones resembling the UV-vis bands of both q-ax and q-eq conformers. Upon vertical excitation, at excited state, q-ax conformer of paraand meta- congeners of pPZPQ and mPZPQ adopt even more planar conformation with dihedral angle between phenothiazine and phenylquinoline planes of 1° (Figure 3). In the meantime, qeq conformers of pPZPQ and mPZPQ adopt flat phenothiazine form with perpendicular geometry between phenothiazine and phenylquinoline moieties with dihedral angle of 89-90°. In excited state, q-ax and q-eq conformers of PZPQ maintained identical perpendicular geometry between phenothiazine and quinoline fragments. The molecular orbital profiles revealed that in the first singlet excited state of q-ax conformers of pPZPQ, HONTO is delocalized throughout the whole phenyl phenothiazine and quinoline system. Meanwhile, HONTO of the q-ax conformer of meta-substituted isomer mPZPQ spreads only over phenyl phenothiazine moiety, apparently, due to the higher extent of π-

conjugation for the *para*-isomer pPZPQ in respect to its *meta*congener. HONTO of q-eq conformers, in the first excited state  $S_1$ , is localized mainly on the phenothiazine fragment. This observation can be explained by the perpendicular geometries between di-*tert*-butyl phenothiazine and phenyl quinoline planes (Figure 3).



**Figure 3.** Optimized geometries of pPZPQ, mPZPQ and PZPQ (B3LYP/6-31G (d, p) in the ground and excited states (S1, T1) along with molecular orbitals (MO) distribution at first singlet and triplet excited states.

Therefore, HONTO of both q-ax and q-eq conformers of PZPQ in excited state is primarily distributed on electron-donating di-*tert*butyl phenothiazine fragment. LUNTO of pPZPQ, mPZPQ and PZPQ in S<sub>1</sub> is strictly localized on phenylquinoline electrondeficient unit. The MO distribution is also different for the excited triplet state (T<sub>1</sub>) of the conformers. The T<sub>1</sub> for all the q-ax conformers of each compound are of the local character where the HONTO and LUNTO are mainly localized on phenylquinoline fragment. Meanwhile, the first excited triplet states T<sub>1</sub> of the q-eq conformers of pPZPQ, mPZPQ and PZPQ are of the charge transfer character where HONTO and LUNTO are localized on electron-rich di-*tert*-butyl phenothiazine and electron-deficient phenylquinoline fragments, respectively.

The energies of S<sub>1, ax</sub> of q-ax conformers are significantly higher and above 3 eV (Table S2). Meanwhile, the S<sub>1, eq</sub> values of the corresponding q-eq conformers are lower by ca. 0.65 eV. All the conformers are characterized by the similar T<sub>1</sub> energies ranging from 2.35 eV to 2.56 eV, which probably stems from the locally exited state of electron donor or acceptor. Therefore, the calculated values of singlet-triplet energy splitting ( $\Delta E_{s-T}$ ) vary significantly along the conformers. Hence, the  $\Delta E_{s-T}$  values of q-ax conformers are considerably higher (0.73–0.84 eV) in comparison with those of the corresponding q-eq conformer with the values of 0.01–0.02 eV.



#### **Photophysical properties**

UV-vis absorption and fluorescence spectra of the solutions of the compounds in the solvents of the different polarities are shown in Figure S4 and Figure 4. Supported by theoretical calculations, experimental absorption spectra of the compounds contain the absorption bands of both phenothiazine conformers (Figure S3). The lowest energy bands (LEBs) of the UV-vis spectra of compounds pPZPQ and mPZPQ correspond to the  $S_0 \rightarrow S_1$  transition (H $\rightarrow$ L) of q-ax conformer. The LEB of UV-vis spectra of mPZPQ corresponds to the  $S_0 \rightarrow S_3$  transitions of q-ax conformer, while  $S_0 \rightarrow S_{1,2}$  transition of q-ax and q-eq conformers are hidden. High-energy absorption bands at 250–274 nm and 300–347 nm are related to the n– $\pi^*$  and  $\pi$ – $\pi^*$  electronic transitions of locally excited di-*tert*-butyl phenothiazine and quinoline derivative (Figure S4).

Two conformations of di-tert-butyl phenothiazine resulted in existence of two excited CT states. Consequently, compounds exhibited dual emissions in solutions and in solid state (Figure 4). Taking into account the results of theoretical calculations and previously reported data,<sup>[28]</sup> the peaks at high energy region can be assigned to the emission of q-ax conformers, while the intensive and dominated peak at low-energy region is attributed to the emission of q-eq conformers. All the compounds showed positive solvatochromism which resulted in bathochromic shifts of photoluminescence (PL) spectra with increasing solvent polarity from toluene ( $\varepsilon$ =2.3) going to the polar dichloromethane ( $\varepsilon$ =8.93) (Table S3).<sup>[29]</sup> Both q-ax and q-eq conformers were found to be sensitive to the increase of the polarity of the media confirming the CT character of the excited states. However, g-eq conformers were much more sensitive to the polarity of the media than the qax conformers with more pronounced red-shifting of the emission (100-130 nm) from toluene to DCM solutions (Table S3). Therefore, the emission intensity of q-eq conformers dropped significantly with increase of the solvent polarity in respect to that of q-ax conformers of pPZPQ, mPZPQ and PZPQ. In the emission spectrum of mPZPQ, the emission intensity of q-ax conformer was much weaker than that of q-eq conformer and could be observed only for the solutions in highly polar CHCl<sub>3</sub> and DCM (Figure 4). Experimental data, in combination with the results of theoretical calculations, confirm the stronger CT character of excited state of q-eq conformers in comparison with that of q-ax conformers. PL quantum yields (PLQY) of the solutions of the compounds in toluene varied from 5% to 13%. D-A compound without  $\pi$ -linker (PZPQ) exhibited the highest PLQY values of both solution and solid sample of 13% and 3%, respectively.

To estimate singlet and triplet energy levels of the compounds, PL and phosphorescence spectra of their solutions in THF were recorded at 77 K (Figure S5). Two well-resolved peaks were observed in PL spectra of the solutions of compounds pPZPQ and PZPQ. However, only single peak was detected in PL spectrum of the solution of mPZPQ. The peaks in high energy region of PL spectra at 77 K of the solutions of pPZPQ and PZPQ can be assigned to the emission of q-ax conformer, whereas the second red-shifted peak can be attributed to the emission of q-eq conformer. Similarly like in PL spectra of the solutions of mPZPQ recorded at room temperature (Figure 4), emission intensity of q-ax conformer in PL spectrum of the solution of mPZPQ recorded at 77 K is negligible.

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Figure 4. Normalized PL spectra of the solutions of (10<sup>-5</sup> M) and of neat films of pPZPQ, mPZPQ and PZPQ ( $\lambda_{exc}$ =350 nm).

The peak in blue region of the spectrum was not detected. Accordingly, the energies of singlet states  $(S_{1, exp})$  of pPZPQ and PZPQ were found to be 3.21 and 3.04, respectively. Due to the observation of single emission peak in the emission spectrum of THF solution of mPZPQ recorded at 77 K, the band is attributed to the singlet emission of q-eq conformer (2.58 eV). In agreement with the results of theoretical investigations, the experimental triplet state energies (T<sub>1, exp</sub>) determined from the onset of the phosphorescence spectra (77 K) ranged from 2.56 eV to 2.59 eV (Table 2). The local excited triplet energies of the phenyl-quinoline electron-acceptor and di-*tert*-butyl phenothiazine electron-donor were similar to those of compounds with the calculated energies of 2.59 eV and 2.64 eV, respectively (Figure S5).

The solid samples of pPZPQ, mPZPQ and PZPQ exhibited single emission peaks at 515, 550 and 554 nm, respectively (Figure S6a, Table 2). Appearance of single peaks at low-energy region of PL spectra of neat films can be attributed to close intermolecular distances which caused the enhanced energy transfer from q-ax conformers with higher excited state levels to the q-eq conformers with lower excited state energies.<sup>[30,31]</sup> Close packing of the molecular conformers in neat films also resulted in concentration quenching which led to the low PLQY of 2–3% and short PL lifetimes in the range of 2.30–38.01 ns (Figure S7, Table S4).

Table 2. Photophysical data for compounds pPZPQ, mPZPQ and PZPQ.								
Compound	λ <sub>PL<sup>[a]</sup> nm</sub>	λ <sub>PL<sup>[b]</sup> nm</sub>	PLQY <sup>[c]</sup> %	PLQY <sup>[a]</sup> %	PLQY <sup>[b]</sup> %	S <sub>1,exp</sub> eV	T <sub>1,exp</sub> eV	
pPZPQ	515	411/525	5	2	15	3.21	2.59	
mPZPQ	550	415/571	7	2	4	2.58	2.57	
PZPQ	554	440/582	13	3	24	3.04	2.56	

 $\lambda_{PL}$  is the PL maxima; PLQY measured for [a] neat films; [b] films of 10% of compounds doped in mCP; [c] toluene solutions (10<sup>-5</sup> M); S1,  $_{exp}/$  T1,  $_{exp}$  are the energies of first excited singlet/triplet states calculated from the onset of PL and phosphorescence spectra of THF solutions (77 K);  $\lambda_{exc}{=}330$  nm;

To reduce concentration quenching and to investigate the nature of each conformer in solid state, compounds pPZPQ, mPZPQ and

in 1:10 ratio. mCP was chosen as the host material due to high energy of the excited triplet state<sup>[32]</sup> as well as convenable overlap between the absorption spectra of the compounds and PL spectrum of mCP (Figure S8). Similarly to the PL of the solutions, dual emission was observed for the doped films (Figure S6a). Unlike the neat films, molecules in doped films experienced higher intermolecular distances which reduced the possibility of energy transfer between the two conformers. Time-resolved PL measurements were carried out to estimate if the compounds exhibit delayed fluorescence. The examination of PL decay curves of the doped films recorded at the wavelengths of emission of each conformer showed that both q-ax and q-eq conformers of para-isomer (pPZPQ) and meta-isomer (mPZPQ) exhibited shortliving component in the range of nanoseconds (Figure S6b, Table S4). Apparently, due to the large  $\Delta E_{S-T}$  value<sup>[33]</sup>, q-ax conformer  $(\lambda_{PL}=440 \text{ nm})$  of compound PZPQ with direct D-A linkage did not exhibit delayed fluorescence either ( $\tau_1$ =0.68 ns,  $\tau_2$ =3.47 ns) (Table S4). PL decay curve of q-eq conformer of PZPQ ( $\lambda_{PL}$ =582 nm) differed and was characterized by double exponential fit with short- and long-lived components. Consequently, short lived component with the lifetime of 23 ns is attributed to the prompt fluorescence, while long-lived component with lifetime of 5.8 µs is ascribed to the delayed fluorescence (Figure 5 (a, b), Table S4). In contrast to the results of the theoretical calculations, the q-eq conformers of pPZPQ and mPZPQ were not characterized by delayed fluorescence. Apparently, the presence of phenyl linker extends conjugation as well as increases quantity of the rotational \_ degrees of freedom between electron-donating di-tert-butyl phenothiazine moiety and electron-accepting auinoline heterocycle. PZPQ containing no linker possesses only one rotational degree of freedom, i.e. the angle between phenothiazine and quinoline units, while pPZPQ and mPZPQ both possess two rotational axes, i.e. those between quinoline unit and phenylene linker and between phenylene linker and phenothiazine unit. This extension of conjugation between electron-donor and acceptor led to the possible molecular configuration with weaker CT state which was enough to quench delayed fluorescence.

PZPQ were doped in 1,3-Bis(N-carbazolyl)benzene (mCP) host

To elucidate the contribution of triplet states to the total emission of PZPQ, PL spectra of air equilibrated and deoxygenated toluene solutions were recorded. Enhancement of the emission intensity by the factor of 2.37 of the peak at 580 nm

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was observed after purging the toluene solution of PZPQ with nitrogen (Figure S9a). The intensity of the peak at 440 nm practically did not change (Figure S9 (insert)).

To examine the nature of delayed fluorescence, the decay kinetics as a function of temperature for PZPQ molecularly dispersed in mCP were studied (Figure S9b). Decrease of the delayed fluorescence lifetime with the increase of the temperature can be observed, which is assigned to the facilitated rISC. The shape and position of PL spectra for the sample at different temperatures remained the same (Figure S9b (insert)). The dependence of intensity of delayed fluorescence as a function of laser pulse energy was investigated to estimate the mechanism of delayed fluorescence (Figure 5c). The slope of c.a. 1, indicates the domination of TADF for q-eq conformer of PZPQ.<sup>[34]</sup>



Figure 5. (a, b) PL decay curves of PZPQ recorded at the emission wavelengths of conformers (c) integrated delayed fluorescence area as a function of the excitation dose ( $\lambda_{exc}$ =350 nm)

#### Mechanochromic properties

The studied compounds showed external force (heating, solvent treatment, mechanical force) responsive photoluminescence (PL). Reversible color variation upon application of external stimuli (grinding, fuming and melting) was observed (Figure 6), Table S5). The as-prepared solids (obtained by recrystallization from isopropanol) of pPZPQ, mPZPQ and PZPQ showed blue and green emission with peaks located at 478, 506 and 519 nm, respectively. Under grinding/melting of the as-prepared samples the emission spectra red-shifted for ca. 30-60 nm and peaked at 538/540 (pPZPQ), 564/569 (mPZPQ) and 569/582 (PZPQ) nm. In all cases, the luminescence color of the meta-stable ground states recovered to that of the stable as-prepared forms by the treatment of ground powders with DCM vapors for 2 min. Interestingly, the emission maxima of single crystals was identical with the emission of as-prepared powders (Table S5). This observation shows that phenothiazine unit of as-prepared powders adopt qeq conformation, confirmed by single crystal X-ray analysis. To get deeper insights into the ML properties and the nature of emissive species, PL decay dynamics and photoluminescence quantum yields (PLQY) of the different forms of compounds pPZPQ, mPZPQ and PZPQ were studied (Figure S10, Table 3, S5). PL decay curves of as-prepared and fumed stable states as well as of single crystals of pPZPQ and mPZPQ were adequately represented by single exponential fits with the lifetimes of 2.2 and 10.4 ns, respectively. The fumed samples of para- and metaisomers showed identical to their as-prepared samples bluegreen emission and the similar PL lifetimes in the range of nanoseconds (2.2/10.6 ns). This observation confirmed the

complete restoration from the meta-stable ground sample to the stable initial one. Surprisingly, upon grinding and melting of asprepared forms, along with the bathochromic shifts of the emission spectra, long-lifetime components appeared in PL decay curves of pPZPQ and mPZPQ (Table 3). Usually, ground and melted samples of compounds experience distortion of the molecular packing accompanied with longer PL lifetimes.<sup>[18]</sup> To our knowledge, these compounds are among the first reported examples of materials exhibiting morphology-dependent mechanically-induced delayed fluorescence. Ground and melted samples of compounds pPZPQ and mPZPQ showed slightly higher PLQY of 3–8% relative to the as-prepared and fumed forms (1–4%) (Table S5).



**Figure 6.** (a) PL spectra and images of different states of compounds (asprepared (i), ground (g), fumed with CH2Cl2 (f), melted (m) and crystallized (c)) ( $\lambda_{exc}$ =350 nm) (b) The images of the samples before and after applying external forces taken under excitation at 365 nm.

PLQY enhancement can be attributed to the activated delayed fluorescence which allows to harvest both singlet and triplet excitons. Unlike compounds pPZPQ and mPZPQ containing phenylene linkage, the as-prepared, fumed and crystalline forms of PZPQ in their PL decay curves showed both prompt (7.1 ns, 9.9 ns and 10.2 ns, respectively) and long-living components (1.7  $\mu$ s, 1.9  $\mu$ s and 1.6  $\mu$ s, respectively). PL decay curves of ground and melted forms of PZPQ also exhibited prompt and delayed components with the lifetimes of 25–26 ns and 1.3–1.6  $\mu$ s, respectively (Figure S10).

Table 3. PL decay characteristics of the samples of pPZPQ, mPZPQ and PZPQ (1st cycle).								
Somolo	pP	ZPQ	mP	ZPQ	PZPQ			
Sample	τ <sub>1</sub> , ns	τ <sub>2</sub> , ns	τ <sub>1</sub> , ns	τ <sub>2</sub> , ns	τ <sub>1</sub> , ns	τ₂, ns		
		TAD	TADF on					
Ground	10.1 (29%)	1579.3 (71%)	33.3 (33%)	1524.1(67%)	25.9 (44%)	1648.1 (56%)		
Melted	9.3 (31%)	1747.7 (69%)	30.3 (27%)	1946.1 (73%)	26.4 (57%)	1317.5 (43%)		
		TAD						
As-prepared	2.2 (100%)	-	10.4 (100%)	-	7.1 (38%)	1703.9 (62%)		
Fumed	2.2 (100%)	-	10.6 (100%)	-	9.9 (20%)	1922.8 (80%)		
Crystalized	2.2 (100%)	-	10.9 (100%)	-	10.2 (34%)	1651.5 (66%)		

 $\tau_{1/}$   $\tau_2$  are the fluorescence lifetimes; The PL decay curves were fitted with residual values of 1.006-1.300

Interestingly, the compounds exhibited stable emission reversibility of as-prepared powders after several grinding-fuming cycles (Figure 7, S11a) without degradation. pPZPQ and mPZPQ demonstrated intriguing stable switching between prompt fluorescence of as-prepared and fumed samples to delayed fluorescence observed under grinding. Stable mechanoresponsive delayed fluorescence on/off was observed during four grinding-fuming cycles (Figure 7b, S11, Table S6).



Figure 7. Reversibility of (a) wavelengths of PL maxima and (b) PL lifetimes of compounds pPZPQ and mPZPQ after five grinding/fuming cycles ( $\lambda$ exc=350 nm).

Likewise, PL of pPZPQ and mPZPQ, the emission of D-A compound PZPQ recovered to the initial one after several grinding-fuming cycles. However, PZPQ showed delayed PL component in all the states obtained after grinding-fuming cycles. Estimation of delayed fluorescence intensity as a function of laser power disclosed the nature of delayed fluorescence of pPZPQ, mPZPQ and PZPQ. The linear plot with a slope of 1 revealed the monomolecular origin of delayed fluorescence, which corresponds to TADF (Figure S12).

The unique property of mechanically switchable TADF can be explained after careful examination of the single crystal and powder X-ray analysis (Figure 8, S13). Single crystal X-ray diffraction analysis revealed the predominance of q-eq phenothiazine conformers of the compounds in the crystalline forms. The torsion angles between phenothiazine and phenylene/quinoline units for pPZPQ, mPZPQ and PZPQ were found to be 85°, 88° and 79°, respectively. The angles between quinoline unit and phenyl linker in pPZPQ and mPZPQ were found to be of 2° and 3° for respectively. Thus, PZPQ containing no phenyl linker can be characterized with only one rotational degree of freedom, i.e. the angle between phenothiazine and guinoline planes (Figure 1b). Meanwhile, pPZPQ and mPZPQ experience more rotational flexibility between donor and acceptor moieties due to the presence of two rotational axes, i.e. those between guinoline unit and phenylene linker and between phenylene linker and phenothiazine unit. Apparently, this extension led to the less efficient CT which was enough to guench delayed fluorescence. For all the different states of the compounds, upon applying of external stresses the color variation of emission occurred due to the changes of morphology between the crystalline and amorphous phases. The as-prepared crystalline samples of the compounds exhibited sharp and intensive diffraction peaks in their powder X-ray diffractograms (PXRD). (Figure S13). The peaks on PXRD graphs disappeared after grinding and melting. This observation indicates the transition to amorphous phase. Fuming of ground powders with DCM vapors resulted in restoration of the as-prepared crystalline phase. The single crystal XRD analysis showed that all the compounds were characterized by CH···π interactions between adjacent molecules in their crystalline lattice (Figure 8) which results in restrictions of the internal rotations. Para- isomer (pPZPQ) experienced slightly

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stronger CH··· $\pi$  interactions with the distances of 2.66 – 2.91 Å than mPZPQ and PZPQ. As a result, the emission of crystalline sample of PZPQ was hypsochromically shifted in comparison to those of mPZPQ and PZPQ.<sup>[35]</sup> Due to the twisted conformations, compounds pPZPQ and PZPQ did not experienced  $\pi$ – $\pi$  stacking interactions in their crystal cells. Interestingly, *meta*-isomer displayed several  $\pi$ – $\pi$  interactions between phenyl quinoline fragments of neighboring molecules (Figure 8) which led to the red-shifted emission band in respect to that of *para*- isomer. Due to the restricted intramolecular rotations caused by CH··· $\pi$  interactions, phenylene linker in pPZPQ and mPZPQ molecules is located in the same plane with quinoline unit.<sup>[36]</sup>



Figure 8. Single crystal molecular structures and molecular packing of (a) pPZPQ, (b) mPZPQ and (c) PZPQ obtained from single crystal X-ray analysis.

Such localization of phenylene ring, apparently, is responsible for the extended conjugation and as a result higher  $\Delta E_{S-T}$  value. Such a molecular geometry presumably results in the decrease RISC efficiency and consequently "turns-off" TADF of pPZPQ and mPZPQ in crystalline phase. After mechanical or thermal treatment (e.g. grinding, melting) the CH···π interactions are eliminated and molecules pack in more condensed matter thus experiencing stronger  $\pi$ - $\pi$  stacking interactions. Molecular fragments in amorphous powders are able to change their torsion angles, which results in the decrease of conjugation followed by reduction of  $S_1$  energy and, thus, decrease of  $\Delta E_{S-T}$  value. This can induce rISC and "turn-on" TADF and make the compounds potential candidates for memory devices with multicoding/recoding abilities (Figure 1b).

#### **Oxygen-sensing properties**

While potential application of compounds pPZPQ and mPZPQ in memory devices (data storage) with multi-coding properties was demonstrated, compound PZPQ containing no phenylene linker and characterized by constant TADF was used as oxygen sensing

probe. The 10 wt% solid dispersion of PZPQ in Zeonex® was prepared for testing oxygen sensitivity of the compound. Zeonex® was used as a rigid matrix to suppress intermolecular interactions <sup>[37–39]</sup> leaving the energy transfer to the molecules of oxygen to be the main path of non-radiative deactivation of excitons and excluding energy transfer between conformers. PL spectra were recorded consecutively under conditions of different nitrogen/oxygen ratio kept for 15 minutes each for the stabilization of intensity. As it is shown in Figure 9a, emission of PZPQ is strongly quenched by oxygen which intercepts the triplet electronic excitation energy. The emission band related to the qeq conformer is considerably more suppressed than that of q-ax conformer even at low portions of oxygen revealing its more expressed TADF character. More specifically, TADF intensity of the q-eq conformer of PZPQ derived from the measurement in a nitrogen environment was found to be by ca. 22.5 times higher than intensity of its prompt fluorescence taken under oxygen flow. At the same time, only two-fold increase was observed for the band related to the q-ax conformer caused by suppressing of the non-radiative exciton deactivation. The respective Stern-Volmer plot<sup>[40]</sup> reflecting suppression of emission with the increase of oxygen concentration in the medium is given in Figure 9b. Io is the intensity of emission recorded under nitrogen atmosphere and I denote the intensity at specific concentration of oxygen. The initial linear dependence caused by a dynamic guenching is followed by a downward curvature started at ~10000 ppm attributed to the partial heterogeneity of the doped film. The so-called Stern-Volmer constant  $K_{SV}=I_0/I-1$  was estimated to be 7.5.10<sup>-4</sup> pmm<sup>-1</sup>. Additionally, the reversibility of oxygen sensitivity of the system was examined taking into account the relatively low adjusted R<sup>2</sup> of 0.91 of the Stern-Volmer plot. After the measurement in air two successive measurements after 35 minutes of exposure of the film under purged oxygen and nitrogen atmosphere, respectively, showed the range of intensities as presented in Figure 9c. All the following cycles had duration of 10 minutes each.



**Figure. 9.** (a) PL spectra, (b) Stern-Volmer plot, (c) PL intensity of 10% solid solution of PZPQ in Zeonex® recorded at room temperature and different ratio of nitrogen and oxygen ( $\lambda_{exc}$ =350 nm).

The reference of 1.5 kppm of oxygen was taken for the test of reproducibility of the same level of intensity at exact portion of oxygen proving the great capacity of oxygen sensing of PZPQ.

#### Conclusions

Structure-properties relationship of the different conformers of new donor-acceptor multifunctional quinoline-phenothiazine conjugates were studied by theoretical and experimental tools. compounds showed unique tunable multicolor The mechanoluminescence. The emission of as-prepared crystalline compounds shifted towards the yellow region by ca. 50 nm after grinding and melting. In all cases, di-tert-butyl phenothiazine fragment of crystalline samples (as-prepared/fumed and single crystals) adopted quasi-equatorial conformation. The change in molecular packing was used as the key for controlling the luminescence mechanism. Controlled on/off TADF was achieved due to transitions between crystalline and amorphous phases. TADF was activated for compounds with phenyl linker under application of external forces (grinding and melting) to the asprepared crystalline samples. The compounds experienced reversible stable switches between prompt fluorescence and TADF after four grinding-fuming cycles. Both crystalline (asprepared/fumed/single crystal) and amorphous samples (ground/melted) of derivative of guinolone and di-tert-butyl phenothiazine having no spacer exhibited TADF. Discovery of compounds with external-force-sensitive delayed fluorescence offer new promising approaches for development of sensing and stimuli-responsive devices as well as provide new directions in development of efficient multifunctional compounds. New application towards memory devices with multi-coding/recoding of multifunctional TADF materials was demonstrated for the compounds containing phenylene linker. The compound containing no phenylene bridge characterized by constant TADF showed oxygen sensitivity with the Stern-Volmer constant of 7.5·10<sup>-4</sup> pmm<sup>-1</sup>.

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New phenothiazine and quinoline derivatives exhibiting outstanding phase-dependant reversibility between ON/OFF stages (low and high emission intensity, drastic shifting of emission colors, short- and long-lived fluorescence) under systematic grinding-fuming cycles required for multichannel memory devices based on optical information multi-coding.