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Tuning Electron-withdrawing Strength on Phenothiazine Derivatives: Achieving 100% Photoluminescence Quantum Yield by -NO₂ substitution

Meng-Chi Chen,^[a] Yao-Lin Lee,^[a] Zhi-Xuan Huang,^[a] Deng-Gao Chen,^[a] and Pi-Tai Chou,*^[a]

M.-C. Chen and Y.-L. Lee made equal contributions.

 M.-C. Chen, Y.-L. Lee, Z.-X. Huang, D.-G. Chen, Prof P.-T. Chou Department of Chemistry National Taiwan University No. 1, Section 4, Roosevelt Road, Taipei 10617 (Taiwan) E-mail: chop@ntu.edu.tw

Supporting information for this article is given via a link at the end of the document.

Abstract: Weak fluorescence (quantum yields < 1% in cyclohexane) of phenothiazine (PTZ) impedes its further utilization. Besides, the nitro group (-NO2) is a well-known fluorescence quencher. Interestingly, we obtained a highly fluorescent chromophore by combining these two moieties, forming 3-nitrophenothiazine (PTZ- NO_2). For comparison, a series of PTZ derivatives with electronwithdrawing groups (EWG) (cyano -CN and formyl -CHO) and electron-donating group (EDG) (methoxy -OMe) group at C3position were designed and synthesized. The EWGs exhibit intensified emission compared with parent PTZ or EDG derivatives. Computational approaches unveil that for PTZ and PTZ-OMe, the transitions are from HOMOs dominated by π orbitals to LUMOs of sulphur nonbonding-mixed π^* orbitals, and hence are partially forbidden. On the contrary, the EWGs lower the energy level of lone pair electrons on the sulphur atom, suppressing the mixing of nonbonding orbital with π^* in LUMO such that the allowed $\pi\pi^*$ transition becomes dominant. This work thus demonstrates a judicious chemical design to fine-tune the transition character in PTZ analogues, making PTZ-NO2 attains unity emission quantum yield in nonpolar solvents.

Introduction

Phenothiazine (PTZ) based derivatives have drawn great attention in a variety of aspects such as pharmaceutical chemistry,^[1] dye-sensitized solar cells (DSSCs),^[2] molecular designs in the thermally activated delayed fluorescence (TADF) molecules,^[3] organic light-emitting diode,^[4] and supramolecular host-guest systems.^[5] PTZ is known as an anthracene-shaped heterocyclic compound with electron-rich nitrogen and sulphur atom in the middle six-member ring (see Scheme 1). Hence, its electron density is more abundant than that of other heterocyclic congeners such as phenoxazine (PXZ), acridine and carbazole.^[3f, 6] Moreover, PTZ could be transformed to various states such as neutral, cation radical and oxygenated sulfoxide forms, providing synthetic perspective especially in pharmaceutical fields.^[7] Such bio-synthetic versatility intrigues us to mull the potential of applying PTZ derivatives in luminescence based bio-sensing. However, the low photoluminescence quantum yields (PLQY) in both solutions

and solids of parent **PTZ** (PLQY = 0.16% in cyclohexane) and its derivatives hamper the pratical applications.^[8] In sharp contrast, replacing sulphur in **PTZ** by the oxygen atom, forming **PXZ**, renders moderate emission yield (PLQY = 2.7% in cyclohexane).^[9] The result manifests the role of sulphur atom in harnessing the emission yields.^[10] Accordingly, the relatively soft sulphur atom may lift the energy of lone pair electrons.Then, the $n\pi^*$ state is in close proximity to the $\pi\pi^*$ state in parent **PTZ**, leading to the state mixing that reduces the transition moment. This, together with the nonplanar of the **PTZ** and hence the twisting motions that enhance the non-radiative decay pathways, may account for the low emission yields for **PTZ** (vide infra).

In this study we report the design and syntheses of PTZ derivatives in an aim to harvest the emission in terms of intensity and energy by harnessing the substituent at the PTZ moiety. Note that this approach is much distinct from the recent studies in which the whole PTZ moiety is used as an electron donating group to construct a D-bridge-A TADF materials.[3a-e] Realizing that the twisting sulphur lone pair electron along the sulphurcarbon bond play a key role; on the one hand, we intend to anchor various electron-withdrawing groups (EWG), including formyl (-CHO), cyano (-CN) and even nitro (-NO₂) functional groups at the meta- position with respect to the sulphur atom to lower the lone pair electron energy via the inductive effect. On the other hand, these EWG are intentionally added in the paraposition of the nitrogen atom on PTZ, rendering a potential for charge transfer (CT) character. We thus anticipate that the CT effect may lean the PTZ moiety toward a planar configuration to suppress the non-radiative twisting effect. For a fair comparison we also synthesized methoxy (-OMe) substituted PTZ to represent the electron-donating group (EDG). As a result, the introduction of EDG and EWG revealed large effect on the luminescence properties, which were also supported by the corresponding theoretical approaches (vide infra). Remarkably, exploiting the nitro group that is conventionally thought to be a good emission quencher, the PTZ-NO2 achieve 100% PLQY in nonpolar solvents. In other words, we also demonstrate how nitro group can act as a fluorescence quencher, and how it cannot.^[11] Detail of results and discussion are elaborated below.

Scheme 1. Chemical structures of PTZ and its analogues modified at C3-position.



Results and Discussion

Synthesis Strategy and Molecular Structure

The chemical structures of the titled molecules are depicted in **Scheme 1**. The brief synthetic routes and experimental conditions are shown in **Scheme 2** and addressed below (see **Supporting information (SI)** for details).

Firstly, PTZ was dissolved in THF and nitrated into PTZ-NO2 with concentrated sodium nitrite aqueous solution in ice bath.^[12] PTZ-CHO was synthesized through a Duff reaction, i.e., the hexamine aromatic formylation, by dissolving PTZ with hexamine in an acetic acid solution and reflux overnight.[13] Further, PTZ-CHO was converted to PTZ-CN via an improved Schmidt conversion^[14] by dissolving purified PTZ-CHO with sodium azide in acetonitrile and addition of triflic acid during fast stirring. The synthesis of PTZ-OMe was performed from a mixture of 4-methoxyaniline and bromobenzene in dry toluene through a palladium-catalysed coupling reaction to yield DPA-OMe (see Scheme 2),[15] which then underwent a ring-closure process by reacting with sulphur and iodine in 1,2dichlorobenzene overnight to yield PTZ-OMe.[12a, 16] All five titled compounds were characterized by ¹H and ¹³C NMR and recorded in Figure S8 to S17. The appearance of five titled compounds were recorded and shown in Figure S7.

Single crystals of **PTZ-OMe**, **PTZ**, **PTZ-CHO**, and **PTZ-NO**₂ had been successfully obtained and analysed with Xcalibur, Atlas, Gemini ultra-diffractometer. Detailed crystallography data were included in **SI**. The crystals of **PTZ-OMe** and **PTZ** are both monolithic with a space group of P2₁/c; the crystal of **PTZ-NO**₂ and **PTZ-CHO** are both orthorhombic with a space group of Pna2₁. **PTZ-NO**₂ has a Herringbone packing,^[17] which indicates that there is a strong π - π interaction between different layers in its solid state.

Scheme 2. Synthesis route of five titled molecules.

Photophysical properties

The steady-state absorption and emission spectra of the titled compounds in three solvents, cyclohexane (CYH), toluene (TOL) and dichloromethane (DCM), are depicted in Figure 1, and the selected photophysical properties are summarized in Table 1. The corresponding spectra using ethanol (EtOH) and acetonitrile (ACN) as solvent are provided in Figure S1. Detailed photophysical properties of titled compounds are tabulated in Tables S2-3. As shown in Figure 1, the absorption peak of the EDG substituted PTZ-OMe around 320 nm with absorption extinction coefficient being lower than 10³ M⁻¹ cm⁻¹ can be ascribed to a $\pi\pi^*$ mixed with certain partially forbidden (vide infra) transition of the PTZ chromophore. Further, the emission peaks of PTZ-OMe are not varied by employing different polarity solvents and show mirror-image emission with respect to the lowest lying absorption band, affirming the locally excited (LE) emissive character with vibronic profile. Similar results can be observed in PTZ with absorption maximum at 320 nm and vibronic progressive emission maximized at 440 nm in all three solvents.

In sharp contrast, as substituted by the EWG at the C3position, PTZ-CN exhibits a red-shifted absorption peak around 340 nm (cf. PTZ). By varying the solvent polarity, the emission peaks of PTZ-CN are observed at 450, 460 and 470 nm in cvclohexane. toluene and dichloromethane solutions. respectively, revealing solvatochromism. The result clearly indicates that the lowest lying electronic transition of PTZ-CN is no longer dominant by the LE transition but incorporates noticeable CT transition. The observation is further supported by introducing formyl and nitro EWGs. For PTZ-CHO, the wavelength of the longest absorption tail (shoulder) is apparently red shifted upon increasing solvent-polarity, showing a typical character of intramolecular charge transfer (ICT) absorption band. Furthermore, the emission peaks are recorded at 470, 510, and 540 nm in cyclohexane, toluene, and dichloromethane solutions, respectively. More impressively, PTZ-NO2, having the strongest electron withdrawing -NO2 group, the emission band is red shifted from 540 nm in cyclohexane to as far as 700 nm in dichloromethane, showing the most prominent excited-state ICT character among the titled compounds. Hence, the strength of ICT effect of non-substituted and substituted PTZ analogies, based on the result of solvatochromism, is increased in the order of PTZ-OMe ~ PTZ < PTZ-CN < PTZ-CHO < PTZ-NO₂, which correlates well with the electron withdrawing strength of the substituent. The transformation from LE to CT character is further supported by the frontier orbital analyses elaborated in the section of computational approaches (vide infra).





Figure 1. Steady-state absorption spectra in extinction coefficient (M^{-1} cm⁻¹) (dashed line) as well as photoluminescence (solid line) spectra of PTZ-OMe, PTZ, PTZ-CN, PTZ-CHO and PTZ-NO₂ in various solvents at room temperature. The red, orange, and green lines represent cyclohexane (CYH), toluene (TOL), and dichloromethane (DCM), respectively. See Table S1 for the selected excitation wavelengths.

The above results, though intriguing, may not be surprising in terms of interconversion between LE and CT states. What is even more important, to our viewpoint, is that the corresponding PLQY increases significantly from EDG to EWG substituted **PTZ**. To our surprise, the PLQY of **PTZ-NO**₂ is nearly 100% in the nonpolar solvents such as cyclohexane, which is in sharp contrast to the rather low PLQYs for **PTZ** (0.16%) or **PTZ-OMe** 10.1002/chem.202000754

(0.29%) in the same solvent (see Table 1). Although there exist some highly polarized or polarizable nitro chromophores which could be guite fluorescent,^[18] it is widely considered that **-NO**₂ is a strong fluorescent quencher owing to its high energy level of nonbonding orbital with lone pair electrons (vide supra). To gain further insight, the fluorescence decay dynamics were measured by time-correlated single photon counting (TCSPC). The photoluminescence decays for all titled compounds in various solvents are shown in Figure S2 to S6 with pertinent data listed in Table 1. As a result, PLQY can be expressed as PLQY = $k_r/k_{obs} = k_r/(k_r + k_{nr})$ where k_{obs} , k_r and k_{nr} denote the experimentally observed decay rate constant, the radiative decay rate constant and the non-radiative decay rate constant, respectively. Combining the acquired PLQYs and kobs experimentally, k_r and k_{nr} can thus be deduced and listed in Table 1. As shown in Table 1, in a qualitative manner, it seems that increase of the electron withdrawing strength of substituent causes the increase of k_r but decrease of k_{nr} . For example, k_r of **PTZ** in cyclohexane solution is calculated to be $2.16 \times 10^6 \text{ s}^{-1}$ which is ~60 times as small as that of **PTZ-NO₂** ($1.31 \times 10^8 \text{ s}^{-1}$). This, together with the large k_{nr} of **PTZ** in cyclohexane (1.35 × 10⁹ s⁻¹), leads to its relatively much weaker emission compared with the electronic withdrawing group substituted PTZ molecules. In fact, k_r of 2.16 × 10⁶ s⁻¹ in **PTZ** manifests its forbidden-like lowest lying transition. Moreover, k_r increases as enhancing the electron withdrawing strength (see Table 1), indicating the more allowed lowest-lying transition. On the one hand, the results imply increasing energy of the forbidden $n\pi^*$ character, which makes the sulphur lone pair electron involved upon increasing the electron-withdrawing strength, proving the concept of lifting the $n\pi^*$ transition (vide supra) that is separated from the $\pi\pi^*$ state. This viewpoint is also supported by the gradually increase of the extinction coefficient for the lowest lying absorption band from EDG (e.g. -OMe, ~500 M⁻¹ cm⁻¹ at peak in cyclohexane) to EWG (e.g. $-NO_2$, $> 10^4 M^{-1} cm^{-1}$ at peak) (**Figure 1**). On the other hand, the decrease of k_{nr} may imply the enhancing planarization the PTZ moiety upon increasing the CT property. Supports of these viewpoints are elaborated in the section of theoretical approach.

Table 1. Experimental and calculated optical characteristics for the titled molecules ^a							
Compound	Absorbance S₀→S₁	Emission $S_1 \rightarrow S_0$	Stokes shift (cm ⁻¹)		Quantum yields / Lifetime ° (ns) k_r (s ⁻¹) / k_{nr} (s ⁻¹)		
	Exp. ^b /Cal. (nm) (<i>f</i>)	Exp. ^b /Cal. (nm) (<i>f</i>)	$\Delta E_{exp}, \Delta E_{calc}$	СҮН	TOL	DCM	
PTZ-OMe	314 / 302 (0.0041)	448 / 426 (0.0084)	9526, 9690	0.29% / 0.38 7.56 × 10 ⁶ / 2.60 × 10 ⁹	0.42% / 0.75 5.63 × 10 ⁶ / 1.33 × 10 ⁹	0.56% / 2.33 2.40 × 10 ⁶ / 4.26 × 10 ⁸	
PTZ	318 / 303 (0.0007)	433 / 420 (0.0080)	8352, 9211	0.16% / 0.74 2.16 × 10 ⁶ / 1.35 × 10 ⁹	0.24% / 0.86 2.80 × 10 ⁶ / 1.16 × 10 ⁹	0.22% / 0.81 2.73 × 10 ⁶ / 1.24 × 10 ⁹	
PTZ-CN	331 / 323 (0.0741)	457 / 443 (0.0559)	8330, 8358	6.6% / 5.07 1.31 × 10 ⁷ / 1.84 × 10 ⁸	11% / 5.52 2.13 × 10 ⁷ / 1.60 × 10 ⁸	11% / 5.99 1.81 × 10 ⁷ / 1.49 × 10 ⁸	
PTZ-CHO	376 / 340 (0.1248)	458 / 461 (0.0988)	4762, 7703	44% / 8.22 5.30 × 10 ⁷ / 6.87 × 10 ⁷	46% / 8.47 5.45 × 10 ⁷ / 6.36 × 10 ⁷	41% / 7.98 5.13 × 10 ⁷ / 7.39 × 10 ⁷	
PTZ-NO ₂	408 / 362 (0.1873)	522 / 496 (0.1694)	5353, 7474	100% / 7.63 1.31 × 10 ⁸ / -	29% / 2.76 1.06 × 10 ⁸ / 2.57 × 10 ⁸	0.54% / 0.24 2.29 × 10 ⁷ / 4.22 × 10 ⁹	

^a Experiments were conducted under room temperature, and calculations were performed with m062x/6-31+g(d,p) in cyclohexane. Exp. denotes the lowest-lying absorption or emission peak wavelengths from experimental results; Cal. denotes the computed lowest-lying absorption or emission peak wavelengths; *f* represents oscillator strengths; ΔE_{exp} stands for the Stokes shift calculated from experimental results; ΔE_{cal} stands for the Stokes shift calculated from computational results; ΔE_{cal} stands for the Stokes shift calculated from computational results; ΔE_{cal} stands for the Stokes shift calculated from computational results; ΔE_{cal} stands for the Stokes shift calculated from computational results. ^b The experimental values are taken from the cyclohexane solutions. ^c Lifetime were measured by TCSPC with excitation wavelength at 360 nm for all five compounds.



Figure 2. (a) Excited-state and ground-state optimized structure. (b) Excited-state optimized HOMO and LUMO orbitals of the titled molecules computed by m062x/6-31+g(d,p) with cyclohexane as solvent. The bending angle (θ) in (a) was defined as the angle intercepted by the two planes bisected from the six carbons on both side of the six-membered ring of **PTZ**.

In sharp contrast to the nonpolar solvent, much decreases of PLQYs for the electronic withdrawing group substituted **PTZ** molecules were observed in polar solvent upon increasing the solvent polarity (see **Table 1**). Especially, for **PTZ-NO**₂, PLQY decreases from 100% in cyclohexane to 0.54 % in dichloromethane. Knowing that the emission of **PTZ-NO**₂ has been red shifted to as far as 700 nm in polar solvent, another non-radiative decay channel, i.e., the quenching of the S₁ state by the overlap with ground-state high-frequency or high-density vibrational modes, is expected to be dominant. This so-called quenching operated by the energy gap law increases with decreasing energy gap, rendering the low PLQY in high polar solvent.^[19]

Cyclic voltammetry analysis

Cyclic voltammetry (CV) analysis was also conducted to verify their intrinsic electronic properties, for which the corresponding CV diagrams are provided in Figure S18 and the numeric data are organized in Table 2. In the CV analysis, Ag/Ag+ (0.01M AgNO₃) electrode was selected as a reference electrode. For working electrode, the oxidation potentials and reduction potential measured using a platinum (Pt) were electrode in dichloromethane and a glassy carbon electrode in dimethylformamide, respectively. Both experiments were conducted with 0.1 M of NBu₄PF₆ and used Pt wire as a counter eletrode. The potentials were further referenced externally to the ferrocenium/ferrocene (Fc+/Fc) couple.

As tabulated in **Table 2**, the recorded HOMO are gradually shifted to the more negative side in the order of **PTZ-OMe** (-4.8 eV) > **PTZ** (-4.9 eV) > **PTZ-CN** (-5.1 eV) \approx **PTZ-CHO** (-5.1 eV) > **PTZ-NO**₂ (-5.2 eV), which is consistent with the overall trend of electron donor capability (EDG > non-substituted > EWG). Moreover, as we computed the energy levels of LUMOs by adding the energy gap of the absorption onset, we obtained the associated values in the order of **PTZ-OMe** (-1.50 eV) > **PTZ-CN** (-2.30 eV) > **PTZ-CHO** (-2.48 eV) > **PTZ-NO**₂ (-2.84 eV) as shown in **Table 2**, which correlated well (in a reverse manner) with the sequence of the HOMO and electron donating capability. However, the modifications in energy levels of LUMOs,

being shifted from **PTZ-OMe** (-1.50 eV) to **PTZ-NO**₂ (-2.84 eV) seem to be more drastic than that of LUMOs, which plays a key factor for in the excited-state mixing. Details are elaborated as follows (vide infra).

Computational approaches

To gain in-depth insight into the electronic transition character of the titled molecules, computational approaches were conducted using time-dependent density functional theory (TD-DFT) on the basis of m062x functional associated with 6-31+G(d,p) basis sets (see SI for details). Although b3lyp is also widely used for computational approaches, the absorbance and emission wavelengths calculated by m062x show less deviation from the experimental result in these charge-transfer organics as tabulated in Table S5. Thus, we provided the result of m062x in manuscript, and attached the results of both m062x (see Table S5) and b3lyp (see Table S6) in SI. The computed energy gaps and the associated frontier orbitals are recorded in Table 1 and Figure 2. After geometric optimization in their ground-states (S₀), the titled molecules all exhibit a bending type geometry owing to the existence of the electron-rich sulphur atom as shown in Figure **2(a)**. However, as we defined the bending angle (θ) as the angle intercepted by the two planes bisected from the six carbons on both side of the six-membered ring of PTZ, there exists a trend toward planarization in ground-state optimized structures, for which the angles are recorded in the order of PTZ-OMe > PTZ > PTZ-CN ≈ PTZ-CHO > PTZ-NO2. The EWG seems to reduce the electron density on the sulphur atom, which decrease the size of its lone pair, causing the decreased bending angle. Moreover, the highest occupied molecular orbitals (HOMOs) of the titled molecules are mainly localized at the middle of PTZ core as shown in Figure S20.

With an aim to investigate their emissive properties, we then conducted the geometric optimization in their lowest lying excitedstate (S₁), and their relative structural characters as well as frontier orbitals are shown in **Figure 2** and **Figure S19** to **S20**, respectively.^[20] As shown in **Figure 2(b)**, while the lowest unoccupied molecular orbitals (LUMOs) of the EDG substituted **PTZ-OMe** and parent **PTZ** are still mainly localized on the **PTZ** core, revealing a LE transition character, the contribution of the non-bonding orbitals of the sulphur atom becomes non-negligible in LUMOs. The results indicate that the lowest lying transition contains mainly $\pi\pi^*$ character overlapping, in part, with certain degrees of non-bonding character from sulphur atom.^[21] This forbidden character in transition is reflected in its small oscillator strength calculated for PTZ-OMe (0.0041) and PTZ (0.0007) as tabulated in Table 1), which is consistent with the experimental result of smaller k_r as well as low absorption extinction coefficient (see Figure 1 and Table 1). In contrast, introducing EWGs on **PTZ** decreases the energy of the π^* orbital of **PTZ**, resulting in its less mixing with the sulphur non-bonding orbital. From another perspective, the EWGs make the substituted six-membered ring mainly contributing to LUMOs, diminishing the mixing between $\pi\pi^*$ and $n\pi^*$ states. Accordingly, LUMOs of EWG substituted analogies (PTZ-CN, PTZ-CHO and PTZ-NO2) have negligible contribution from sulphur atom, and the net results reveal CT character.

Combining the above results, the rationalization of the transformation from LE to CT character may be offered in a quantitative manner based on the Marcus-Weller equation expressed below (eq. 1) to deduce the associated free energy (ΔG) of charge transfer in the excited-state.^[22]. The equation is listed below:

$$\Delta G = E_{ox}^D - E_{red}^A - E_{00} - \left(\frac{e^2}{4\pi\varepsilon_0\varepsilon_s r_c}\right) - \left(\frac{e^2}{8\pi\varepsilon_0}\right) \left(\frac{1}{r_{D^+}} + \frac{1}{r_{A^-}}\right) \left(\frac{1}{\varepsilon_{DCM}} - \frac{1}{\varepsilon_s}\right) \quad (\text{eq. 1})$$

where $E_{ox}(D)$ and $E_{red}(A)$ are the oxidative and reductive potential, respectively, measured by cyclic voltammetry; E_{00} are recorded from the 0-0 transition of the titled molecules where charge transfer process start to take place; ε_0 , ε_s , and ε_{DCM} are dielectric constants in vacuum, desired solvent and dichloromethane, respectively; r_c are recorded the distance between donor and acceptor; r_{D^+} and r_{A^-} are the ionic radii of donor and acceptor, respectively. The definitions of r_c , r_{D^+} , and r_{A^-} are visually shown in **Figure S21**. Though it is not common to adapt this equation that were originally designed for photoinduced electron transfer (PET) to the charge transfer (CT) case, the results are quiet convincing in a qualitative manner.

Employing all the recorded values to eq. 1, the corresponding ΔG for undergoing charge transfer are recorded in **Table 2**. Accordingly, ΔG for the titled molecules are in the order of **PTZ** (3.16 kcal/mol) > PTZ-OMe (2.01 kcal/mol) > PTZ-CN (-8.77 kcal/mol) > PTZ-CHO (-13.69 kcal/mol) > PTZ-NO2 (-21.22 kcal/mol). It is thus reasonable to expect that the exergonicity of the titled molecules undergoing charge transfer follow the order of PTZ-OMe ≈ PTZ < PTZ-CN < PTZ-CHO < PTZ-NO₂. Additionally, it is worth to note that the uncertainty of this assessment should be appreciable in recording the emissive energy gap in solution and CV potentials. Also, the definition of r_{D^+} and r_{A^-} is ambiguous, which is only localized at the donor and acceptor sites. Nevertheless, **PTZ-OMe** and **PTZ** possess positive ΔG , which indicates that the CT process is thermodynamically unfavourable, consisting with their LE emission concluded experimentally. On the contrary, the experimentally estimated ΔG of the EWG substituted PTZ analogies are all negative, indicating the accessibility of CT process and resulting the CT emission. The trend of the exergonicity consists with the experimental results.

Last but not the least, it is worth to note that upon geometric optimization in their excited states, **PTZ** core undergoes certain degrees of excited-state structural planarization to enhance its π -conjugation.^[3c, 23] For example, as shown in **Figure 2(a)**, the bending angles (θ) of the titled molecules in ground-state are in the order of **PTZ-OMe** (33.97°) > **PTZ** (33.80°) > **PTZ-CN** (31.73°) **PTZ-CHO** (31.76°) > **PTZ-NO**₂ (30.55°), whereas the bending

angles of the titled molecules are **PTZ-OMe** (12.03°) > **PTZ** (4.45°) **PTZ-CN** (4.68°) > **PTZ-CHO** (0.07°) > **PTZ-NO**₂ (0.03°) in the lowest lying excited-states (S₁), which follows the similar trend, but with a significantly smaller value. This is a general observation in **PTZ** and other heterocyclic derivatives such as phenazine.^[20] Accordingly, the more planar configuration upon increasing the electron withdrawing ability (see **Figure S19**) gives less twisted motion, and hence the decrease of non-radiative decay rate (k_{nr}), rationalizing the ~100% PLQY for **PTZ-NO**₂ in the nonpolar solvent.

Table 2. Electrochemical properties and free energy of photoinduced electron transfer of the three titled molecules with charge transfer. ^a							
Compound	E_{ox}^D	E^A_{red}	HOMO ^b	LUMO ^b	ΔG ^c	-	

Compound	(V)	E _{red} (V)	(eV)	(eV)	kcal/mol
PTZ-OMe	0.49	-2.12	-4.80	-1.85	2.01
PTZ	0.63	-2.02	-4.94	-1.99	3.16
PTZ-CN	0.83	-2.12	-5.14	-2.19	-8.77
PTZ-CHO	0.80	-1.68	-5.12	-2.16	-13.69
PTZ-NO ₂	0.84	-1.00	-5.16	-2.20	-21.22

^a E_{ox}^{D} and E_{red}^{A} are anodic and cathodic peak potentials using Fc+/Fc as reference. ^b HOMO = $-(4.8 + E_{ox}^{D} - E_{ox}^{Fc})$ and LUMO = HOMO + E_{onset}^{PL} , where E_{onset}^{PL} is the energy converted from onset of the locally excited emission from PL spectra, which is 420 nm is our case. ^c Free energy, Δ G, is calculated by eq. 1 based on Marcus-Weller equation.

Conclusion

In conclusion, a series of PTZ analogies were strategically designed and synthesized in an aim to boost the emission intensity. PTZ and the EDG substituted PTZ-OMe exhibit partially forbidden transitions because of the mixed $\pi\pi^*$ and $n\pi^*$ (sulphur nonbonding orbital) states. This, together with nonplanar structure that activates the twisting non-radiative deactivation, rationalizes their weak emission. Conversely, introducing EWGs lowers the energy level of LUMO and diminishes the mixing of nonbonding orbitals to facilitate the allowed π - π * transition. Also, the EWGs substitution induces excited-state charge transfer, which suppresses the twisting non-radiative deactivation to enhance the emission. Among them, a widely considered fluorescence quencher functional group (-NO₂) was also employed in this work. PTZ-NO₂ exhibits 100% Q.Y. in nonpolar solvents (e.g., cyclohexane), which also shows significant solvatochromism in polar solvents, covering the visible region from 500 to 700 nm.

Experimental Section

Synthesis

The characterizations of all compounds are provided in **Supporting** Information.

Absorbance

Absorbance were measured with the double-beam spectrophotometer (U3310, manufactured by Hitachi). Two quartz cuvettes with dimensions of $1 \times 1 \times 4.5$ cm were cleaned with acetone, dried by heat gun, and whipped with acetone-damped Kimwipe. In the sample compartment of, both

reference slot and sample slot were placed with quartz cuvette, and filled with desired solvent to half-full. Parameters, set in Method section of the program, were configured to allow U3310 to scan from 900 nm to 300 nm at a 600 nm/min speed. Then, the sample that was dissolved in desired solvent in advanced was added into the cuvette in the sample slot. The absorbances at intend excitation wavelength, usually around the first absorption peak (longest in wavelength), was adjusted in a range of 0.10 to 0.11 for quantum yield analysis. For lifetime measurement and better absorption and photoluminescence spectrum, the absorbance was adjusted about 0.30.

Photoluminescence

Photoluminescence was recorded with FS980, manufactured by Edinburgh Instruments. Before experiment, lamp and detector cooler of FS980 were turned on, slits were set at desired values, and suitable filter were selected to reduce second harmonic signal. Sample dissolved in desired solvent with reasonable concentration were placed in FS980. Excitation wavelength were chosen at the peak wavelength of the first absorption peak, as listed in Table S1. For example, PTZ has its absorption spectrum peaks at 318 nm when using cyclohexane as solvent. Therefore, the concentration was adjusted by U3310 making the absorbance at 320 nm in a range of 0.10 to 0.11. In FS980, photoluminescence was excited at 320 nm, and scanned from 310 nm to 630 nm, which included the excitation peak to ensure its correct, and 630 nm was 10 nm less than twice of the excitation wavelength to avoid second harmonic signal. To scan beyond 630 nm, a 380 nm long-pass filter was placed between the sample and the detector to block the excitation light scatters entering to the detector to avoid second harmonic signal.

Quantum yields

Quantum yields were measured with comparative method. Suitable standard dyes that possess emission at similar wavelength band to the sample were chosen. In this work, POPOP (RN 1806-34-4), C480 (RN 171615-15-9) and DCM (RN 51325-91-8) were selected as standard dyes. The absorbance spectra and photoluminescence spectra of dyes and sample were both measured under the same condition (temperature, slit, filter, etc.).

Time-Correlated Single Photon Counting (TCSPC)

A 532 nm 80 MHz green pulse laser was generated by Millennia eV (manufactured by Spectra-Physics), a DPSS (diode-pumped solid-state) laser. The laser then passed through Tsunami (manufactured by Spectra-Physics), a flexible, high performance, ultrafast Ti:Sapphire oscillator, which offered the tuning range of 700 nm to 1080 nm. We used the 720 nm to generate the second harmonic frequency at 360 nm for the experiments in this work. 80 MHz of pulse laser only allowed a measurement window of 12.5 ns; therefore, the 80 MHz 360 nm pulse laser then passed through Model 3980 (manufactured by Spectra-Physics), a pulse-selector that could reduce the frequency down to 8.0 MHz. Samples were dissolved in desired solvent with proper concentration (absorbance around 0.3 at excitation wavelength) and put into the sample holder. The laser passed through several adjusting mirrors and illuminated the sample. Emission was collected at a 90° angle with respect to the laser, and a 420 nm long-pass filter was placed between the sample and the detector. MCP-PMT (microchannel plate photomultiplier tube), R3809U-50 (manufactured by Hamamatsu Photonics, assembled by Edinburgh Instruments) detectors were employed in this work. The collected data were fitted by Edinburgh's software.

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Keywords: phenothiazine • nitro • quantum yield • fluorescence.

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Entry for the Table of Contents



A series of C3-substituted phenothiazine (**PTZ**) with different electron-donating and -withdrawing groups was investigated by comprehensive computational approaches and photophysical measurements. Among them, a nitro group substituted **PTZ** possesses 100% quantum yields in nonpolar solvent. The results validate that the interplay of the nonbonding orbital of sulphur atom in **PTZ** plays a crucial role in the electronic transition.

Institute and/or researcher Twitter usernames: @edchen1240