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Mono-Heteroatom Harnessing Excited-state Structural

Planarization for Dihydrodibenzo[a,c]phenazines

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Dedication ((optional))

Abstract: In an aim to generalize the structure-properties relationship of bending heterocyclic molecules that undergo prominent photoinduced structural planarization (PISP), a series of new dihydrodibenzo[a,c]phenazine derivatives with one nitrogen atom (N) replaced with oxygen (PNO), sulfur (PNS), selenium (PNSe) and dimethylmethanediyl (PNC) moieties were strategically designed and synthesized. The representative molecules PNO. PNS and **PNSe** reveal significant nonplanar geometries in the ground state, which undergoes PISP, yielding a planar-like conformer hence a large Stokes-shifted emission. The combination of femtosecond early relaxation dynamics and computational approaches establish a $\mathsf{R}^*\!\!\to \mathsf{I}^*$ (intermediate) $\to \mathsf{P}^*$ sequential kinetic pattern for **PNS** and **PNSe**, while differently **PNO** undergoes $R^* \rightarrow P^*$ one-step kinetics. The polarization ability of the substituted heterosubstituted atoms, being in the order of O < S < Se, correlates their increase of π conjugation and hence the Stokes shift of the emission, being in the order of PNO < PNS < PNSe. PNSe with largest PISP barrier was proven to be a highly sensitive viscosity probe. Further evidence for 6A family heteroatom harnessing PISP is given by PNC, in which the dimethylmethanediyl substituent lacks lone pair electrons for π extension, yielding a normal emission of the bent structure. The results lead us to conclude that PISP is ubiquitous in dihydrodibenzo[a,c]phenazines, for which the driving force is to elongate the π -delocalization, gaining stabilization in the excitedstate.

Introduction

Owing to the multiple potential applications, anomalous electronically excited-state phenomena for molecules, resulting from distinct geometries between ground and electronically excited states, have drawn considerable attention.¹⁻¹³ Upon excitation, geometry changes such as *cis-trans* isomerization,¹⁴⁻ proton-transfer tautomerization,18-22 and conformational

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planarization give rise to fascinating optical phenomenon.¹⁻⁶ As for photoinduced structure planarization, one well-investigated process is twisted-to-planar motion resulted from the aromatic ring rotation through the single bond.¹¹⁻¹³ The other is ascribed to an emerging class of non-planar heterocyclic molecule N.Ndiphenyl dihydrodibenzo[a,c]phenazine (DPAC, see in Scheme 1) and its derivatives, which displayed a photoinduced structural planarization (PISP) process, resulting in a large Stokes-shifted red emission (ca. 610 nm for DPAC) despite their absorption in the UV region.^{1,4-6} The proposed PISP mechanism incorporates the conformational planarization of the bent-shape heterocyclic molecule along with the N-N axis, followed by the relaxation of steric strain via the rotational N-aryl ring to establish a $R^* \rightarrow I^*$ →P* sequential kinetic pathway where R* state is the originally prepared state, I* is the intermediate state with a partially relaxed structures that reduces strain between N,N-biphenyl and dihydrodibenzo[a,c]phenazine moiety prior to proceed with the planarization. The P* state shows a planarized core chromophore such that the π -electrons are more delocalized. Therefore, the $\pi\pi^*$ energy gap in P^{*} is significantly reduced (cf. R*) rendering anomalously large Stokes shifted emission. Recently, steric effect toward DPAC systems has been probed, which showed DPAC derivatives could be tuned from bent to planar configuration in the ground state simply by introducing methyl substituents to harness the steric strain.⁶ Scheme 1. Chemical structures of N-aryl acridine analogues.



In an aim to generalize the structure-PISP relationship, we then mull the requirement of molecular identity for PISP by asking what if replacing the dihydrophenazine with other heterocyclic heterosubstituted cores. can the dihydrodibenzo[a,c]phenazines systematically harness PISP in both kinetics and thermodynamics. To attain this goal, in this nitrogen in N,N'-diphenyl studv. we substituted one dihydrodibenzo[a,c]phenazine with other elements, including selenium and dimethylmethanediyl, oxygen, sulfur, and

PNSe

synthesized a series of new molecules **PNO**, **PNS**, **PNSe** and **PNC**, respectively (see **Scheme 1**), while the steric hindrance between *N*-phenyl ring and phenanthrene ring is retained to make the photophysical behavior fairly comparable. These substituted elements exhibit versatile chemical properties, such as covalence radius, electronegativity and a wide range of oxidation states,²³ which make possible the exploration of the structure-PISP relationship, among them, the size of the substituted element is considered to have the direct effects regarding to the π -conjugation and the diffusive ability of the electrons. Detail of results and discussion is elaborated as follows.

Results and Discussion

2.1 Design and synthesis.

Inspired by the chemical structure of DPAC, a new series of heterocyclic conjugated molecules PNX (see Scheme 1, X represent for O, S, Se and C atoms) were designed and synthesized. We attempted to tune the flexible degrees of the bent heterocyclic skeleton by introducing different atoms into the system. Chemical structure and synthetic procedure of the title molecules are shown in Scheme 2. In brief, two intermediates, dibenzo[a,c]phenoxazine (2-2) and dibenzo[a,c]phenoselenazine (4-3), were synthesized by reductive deoxygenation of the corresponding nitrobiphenyl derivatives with excess triphenyl phosphine according to the modification of Cadogan reaction.²⁴ ²⁵ 14H-dibenzo[a,c]phenothiazine (3-2) was prepared form Nphenylphenanthren-9-amine using the classical condensation by fission with powder sulphur.²⁶ 9,14-dihydroacridine ring (1-3) was achieved by cyclization of the corresponding tertiary alcohol derivative that was prepared via Grignard reaction from methyl magnesium bromide and methyl 2-(phenanthren-9ylamino)benzoate.27 The target molecules, N-aryl acridine

derivative **PNC** and other three chalcogen-substituted compounds (**PNO**, **PNS**, **PNSe**), were synthesized via the Buchwald-Hartwig reaction of bromobenzene and corresponding substituted amine analogues (see **Scheme 2**).²⁸⁻³⁰ The detailed work-up processes are elaborated in the Supporting Information (**SI**). All structures of these target compounds were fully characterized by ¹H NMR, ¹³C NMR, high-resolution mass spectrometry (HRMS) (see **SI**) and further confirmed by single crystal X-ray diffraction analysis described below. **2.2 Crystal Structure.**

Figure 1 depicts the single crystals of PNX (X represent for O, S, Se and C atoms) series from three viewing angles. All the four compounds exhibit a nonplanar molecular geometry with a folded phenyl ring, which closely resembles the conformation as observed in DPAC. It can be seen from the front view in Figure 1 that four molecules displayed a bent boat shaped central heterocyclic core with the bending angle Θ_a ($\angle N$ -X-C15... $\angle N$ -X-C21, X represents O, S, Se and C) ranging from 131° to 143°. Meanwhile, the central heterocyclic ring in the four compounds is folded to the N-substituted phenyl along the N···X (O, S, Se and C) axis, yielding a bent angle of 109~116°. This nonplanar conformation is due to the large steric interaction between the Nsubstituted phenyl ring and phenanthrene ring.⁴⁻⁶ Other than the similar molecular skeleton, a noticeable conformational difference among the three chalcogen-substituted compounds (**PNO**, **PNS**, **PNSe**) lies in bending angle Θ_a , accompanied with twisted degree between central core and N-substituted phenyl ring. The Θ_a of PNS and PNSe were recorded as 134° and 131°, respectively, while that of PNO was added up substantially to ~143°. Obviously, the substituent effect of the inserting chalcogen heteroatoms make a significant structural difference. In addition, the bond angle Θ_b (\angle C14-N-C21) increases from 111° for PNO to 116° for PNSe along with bond angle Θ_c (\angle C15-X-C16, X represent for O, S, Se and C) change from 113° to 95°,

Scheme 2. Synthetic routes of N-aryl acridine derivative PNC and three chalcogen-substituted analogues (PNO, PNS, PNSe).



which is presumably due to the increased atom radius. All the results imply that replacing nitrogen of **DPAC** with chalcogen and carbon leads to diverse molecular conformations, providing versatile molecular characteristics.



Figure 1. Single crystal structure of (a) PNO, (b) PNS, (c) PNSe and (d) PNC from three angles of view. The bending angle between planes 1 (C15, X, and N, X represent for O, S, Se and C) and 2 (C21, X, and N) is denoted as Θ_a for all title compounds. Note that under this definition, a bending angle of 180° specifies the planarization between planes 1 and 2, while 0° indicates two parallel planes. Accordingly, from 0 to 180°, a larger bending angle indicates more planarization. The bond angles \angle C14-N-C21 and \angle C15-X-C16 are denoted as Θ_b and Θ_c , respectively.

2.3 Steady state properties.

Figure 2 depicts the normalized absorption (in toluene) and emission spectra of the **PNX** molecules in various solvents. The selected photophysical properties are summarized in **Table 1** and **Table S1**. The lowest lying absorption band for all the title molecules are located at 330-400 nm, which originates from the charge transfer-like transition associated with the *N*-phenyl ring (HOMO) and the corresponding phenanthrene rings (LUMO), as verified by the computational approaches (*vide supra*). The results affirm that all **PNXs** have a similar core chromophore in their ground-state, and their < 400 nm absorption onset infers a bent dihydrodibenzo[*a*,*c*]phenazine that lacks extended- π conjugation, consistent with their crystal structures.

Despite the similarity in absorption profiles, the studied molecules exhibit distinct photoluminescence properties. The fluorescence peak wavelength of **PNO** was observed at 465 nm with a large Stokes shift of 7,906 cm⁻¹. Here, the Stokes shift is defined as the difference in wavenumber between the lowest absorption and emission peak frequencies. **PNS** and **PNSe** show even further red-shifted emission maximized at 555 nm and 570 nm and the Stokes shift as large as 11,480 and 11,955 cm⁻¹, respectively, in toluene. Notes that **PNSe** also reveals a small but non-negligible normal Stokes shifted emission band at 429 nm, which resembles those observed in **DPAC (Figure 2e)**,⁴ inferring a perhaps slow structural relaxation process, which will

be unveiled in the time-resolved studies. Finally, in sharp contrast, **PNC** exhibits an emission maximum at 417 nm with a normal Stokes shift of $5,313 \text{ cm}^{-1}$.



Figure 2. Steady-state absorption in toluene solution (black dash line) and photoluminescence spectra (solid line) of (a) PNO, (b) PNS, (c) PNSe, (d) PNC and (e) DPAC in various solvents at room temperature. Notes that blue, green and red color represent cyclohexane, toluene and dichloromethane solutions, respectively. Inset: room-in picture of PNSe and DPAC within 400 to 500 nm and 370 to 500 nm wavelength region, respectively. (f) The visualized emission color of PNC, PNO, PNS and PNSe excited by an UV lamp (365 nm).

Because the emission peaks are subject to either very small (in PNO) or even negligible (in PNS and PNSe, see Figure 2) solvent polarity dependence, the large Stokes-shifted emission properties caused by solvatochromism can be ruled out.³¹⁻³⁴ Alternatively, owing to their bent geometries, we thus propose the occurrence of PISP for PNO, PNS and PNSe to elongate the π -conjugation, giving the anomalously large Stokes-shifted emission. An indirect support of this proposal is given by the photoluminescence properties of PNO, PNS and PNSe in solid, shown in Figure S9. For all three compounds, the corresponding emission shows only one dominant emission band with normal Stokes shift. In the solid, the imposed environment force forbids the occurrence of PISP; therefore, PNO, PNS and PNSe exhibit normal emission of the bent structure. Further evidence is provided in the following time resolved measurement and theoretical approaches. 2.4 Time-Resolved Emission Spectroscopy.

We then performed comprehensive spectral/dynamic analyses using the nar to gain further insights into the related photophysical properties (TCSPC) in co **Table 1.** Experimental and Calculated Optical Characteristics for the Title Molecules in Cyclohexane.

using the nanosecond time-correlated single photon counting (TCSPC) in combination with the femtosecond fluorescence ups in Cyclohexane.

| | | Absorption $S_0 \rightarrow S_1$ | | Emission S0→S1 | | | Stokes shift (cm ⁻¹) | | 0 Y | r (nc) ^c | |
|----|------|----------------------------------|----------------------|----------------|---------------------|----------------------|----------------------------------|----------------------|-----------------------|---------------------|---------|
| | | $\lambda_{exp}(nm)$ | $\lambda_{calc}(nm)$ | f | $\lambda_{exp}(nm)$ | $\lambda_{calc}(nm)$ | f | ΔE_{exp}^{b} | ΔE_{calc}^{b} | - Q. I. | ų (IIS) |
| 1. | PNO | 340 | 358 | 0.1190 | 465 | 534 | 0.0909 | 7906 | 9206 | 0.35 | 8.17 |
| 2. | PNS | 339 | 374 | 0.0496 | 555 | 642 | 0.0572 | 11480 | 11162 | 0.17 | 14.46 |
| 3. | PNSe | 337 | 371 | 0.0264 | 570 | 687 | 0.0494 | 11955 | 12428 | 0.02 | 3.21 |
| 4. | PNC | 338 | 375 | 0.0523 | 412 | 482 | 0.0350 | 5313 | 5931 | 0.19 | 4.24 |

^aData were recorded in cyclohexane at room temperature. λ_{exp} = experimental lowest-lying absorption or emission wavelengths, λ_{calc} = calculated lowest-lying absorption or emission wavelengths *f* = oscillator strengths, ΔE_{exp} = experimental Stokes shift, ΔE_{calc} = calculated Stokes shift, Q.Y. = emission quantum yield, τ_{f} = population decay time.

^bThe experimental and calculated values are calculated from the energy difference between absorption and emission wavelengths, respectively.

^cThe population decay time constants, which are measured by time correlated single photon counting (TCSPC, see text).

conversion techniques. Table S1 lists the nanosecond dynamics of the fluorescence decay kinetics of title molecules in various solvents at 298 K by TCSPC. Due to the low solubility of PNSe in cyclohexane, we conducted all femtosecond fluorescence upconversion measurements in the toluene solution. Here, it is worthy of noting that the fluorescence population decays for some of the studied compounds are longer than several ns. To avoid the repeated emission accumulation by conventionally high-repetition-rate (8-80 MHz) femtosecond laser, a low repetition rate 1kHz femtosecond laser system was used as the pump-probe source for the fluorescence up-conversion measurements (see Supporting Information for details). In this study, under 380 nm excitation and monitoring at the entire emission region of the steady-state emission, the results for PNSe and PNO were recorded in Figure 3 with pertinent data tabulated in Table 2 and 3, respectively. Also, the results for PNS are shown in Figure S10 and Table S2 of the supporting information.



Figure 3. Femtosecond fluorescence transients (open circles) of (a) **PNSe** and (b) **PNO** in toluene at room temperature observed at various wavelengths as depicted. The black solid lines in figure denotes the instrument response function (IRF). The fitting results are tabulated in **Table 2** and 3. Note that (a) and (b) are depicted with different time windows, being 20 ps and 10 ps, respectively.

We first use **PNSe** to present the results and discussions. Notes that the 380 nm excitation is selected due to its near onset of the lowest lying transition to avoid the possible interference from highly vibronic relaxation.³⁵⁻³⁸ Upon monitoring at a short wavelength region, e.g. 420 nm, the relaxation kinetics consists of a resolvable fast decay component can be fitted to be 1.2 ps, followed by a relatively slower component of 7.8 ps. Increasing the monitored wavelength from 460 to 500 nm both 1.2 and 7.8 ps decay components gradually decrease and become the rise components. However, the rising component at e.g. 500 nm, which has rather small steady-state intensity, becomes fast (~2.0 ps). This is due to the cancellation between rise of decay in this wavelength, which is supported by extending the monitored emission to 570 and 600 nm. It then becomes clear a 7.8 ps rise component, followed by a long population decay that seems to be constant within the acquisition window of 20 ps. This long population decay component was further measured TCSPC and fitted to be 3.2 ns (Table 1). Similar kinetic patterns were obtained for PNS in toluene (see Figure S10 and Table S2), except that the early fast decay component was fitted to be 1.0 ps, the other two time constants were fitted to be 4.4 ps and 12 ns.

The above fluorescence up-conversion data are reminiscent of the planarization kinetics on **DPAC**, and thus the entire relaxation kinetics of **PNS** and **PNSe** can be described by a sequential kinetic pattern expressed as: ⁴⁻⁵

 $R^* \xrightarrow{\tau_1} I^* \xrightarrow{\tau_2} P^* \qquad (1)$

where R* represents the initial Franck-Condon excited state, I* is an intermediate with the local minimum energy, and P* is the global minimized state after the structural relaxation (i.e. planarization). As for **PNSe** the R* \rightarrow I* and I* \rightarrow P* processes exhibited the time constants of 1.2 ps (τ_1) and 7.8 ps (τ_2), respectively, followed by a population decay of the P* state of 3.2 ns.

 $\mbox{Table 2.}$ Fitting Results of Femtosecond Fluorescence Up-conversion Measurement for PNSe in Toluene. a

| PNSe | Relaxation time constants | | | | |
|-----------------|---------------------------|-----------------|----------------|--|--|
| λ_{amo} | τ ₁ | τ ₂ | $\tau_{\rm f}$ | | |
| 460 nm | 1.20 ps (0.52) | 7.80 ps (0.48) | - | | |
| 500 nm | 1.20 ps (0.18) | 7.80 ps (0.82) | - | | |
| 540 nm | 1.20 ps (-0.21) | 7.80 ps (0.54) | 3.32 ns (0.25) | | |
| 580 nm | 1.20 ps (-0.47) | 7.80 ps (0.00) | 3.32 ns (0.53) | | |
| 620 nm | 1.20 ps (-0.50) | 7.80 ps (-0.05) | 3.32 ns (0.45) | | |

 $^a\text{The time constant }\tau f$ of the population decay is determined from the TCSPC results and is used to the fitting up-conversion signals.

Table 3. Fitting Results of Femtosecond Fluorescence Up-conversion Measurement for PNO in Toluene. $^{\rm a}$

| PNO | Relaxation time constants | |
|---------------------|---------------------------|----------------|
| λ_{amo} | τ ₁ | τ _f |
| 420 nm | 0.62 ps (0.33) | 7.68 ns (0.67) |
| 460 nm | 0.62 ps (-0.44) | 7.68 ns (0.56) |
| 500 nm | 0.62 ps (-0.42) | 7.68 ns (0.58) |
| 540 nm | 0.62 ps (-0.38) | 7.68 ns (0.62) |
| 580 nm | 0.62 ps (-0.35) | 7.68 ns (0.65) |
| â z ı ı: | | · |

^aThe time constant τf of the population decay is determined from the TCSPC results and is used to the fitting up-conversion signals.

In comparison to **PNSe** and **PNS**, the fluorescence relaxation dynamics for **PNO** is distinct. Upon monitoring at the onset region of 405 nm, the emission consists of a fast but resolvable decay component fitted to be ~0.6 ps. Increasing the emission wavelength, this 0.6 ps decay becomes the rise component. However, unlike **PNS** and **PNSe** no relatively long rising component of few ps or longer can be resolved. Upon monitoring at the red tail of emission of 580 nm, the rise

component is fitted to be 0.6 ps that is the same magnitude as the initial decay monitored at 405 nm, followed by a very long population decay, which was resolved to be 7.7 ns by the TCSPC technique (see **Table S1**). In brief, for **PNO** only two time constants can be resolved, 0.6-0.7 ps and 7.7 ns. Accordingly, within the experimental error, the decay component of the 420 nm emission correlates well with rise of the 580 nm emission. Hence, we are able to conclude that the result for **PNO** unveils a precursor (reactant) – successor (product) type of kinetic pattern expressed as:

 $R^* \xrightarrow{\tau} P^*$ (2)

in which the time constant for $R^* \rightarrow P^*$ process is measured to be 0.6 ps (τ), followed by a population decay of the P* state of 7.7 ns.

Finally, with dimethylmethanediyl substitution, **PNC** that exhibits a regular normal emission, shows a system response rise time (<150 fs) and a population decay time of 4.64 ns in time-resolved measurements (see **Table S1**). The results imply that the substituent effect of chalcogen elements play an important role in affecting the excited-state planarization process. Insight into the differences will be discussed in the following computational approaches.



Figure 4. (a) and (b) The frontier molecular orbital contours of the title molecules in optimized ground-state and excited-state geometries, respectively. (c) The optimized geometries of **PNC** in ground-state and excited-state, respectively. (d) The structural relaxation of **PNO** in the electronically excited state. R* represents the initially prepared state, and P* denotes the final planarization state with the global minimum energy along the structural relaxation process. Notes that the structural parameters Θ_a , Θ_b and Θ_c are recorded in the figure, respectively.

2.4 Computational Approaches

The steady-state and time-resolved measurements clearly support the concept that various degrees of excited-state structural relaxation patterns of the studied molecules may depend on different substituted chalcogen elements. Herein, the computational approaches were performed to provide complementary support for experimental results. The geometries optimization of the ground state for the title molecules were carried out through the density functional theory (DFT) method. The electronically excited-state structures with relevant photophysical properties were computed by the time-dependent density functional theory (TD-DFT) method with a B3LYP hybrid function at 6-31+G(d,p) level incorporated with a polarizable continuum model (PCM) (see the computational approaches in SI for details). We also employed CAM-B3LYP and M062X hybrid functions to make a fair comparison among various computational results: pertinent data were tabulated in Table S3. As shown in Table S3, the calculated data, in terms of e.g., energy gaps of absorption and luminescence, are mutually varied by using different functional and basis sets. The computed wavelengths for absorption and emission are in a trade-off. For example, the calculation based on B3LYP functional most closely reflects the onset of the experimental results, whereas its calculated emission has been deviated. Conversely, CAM-B3LYP functional renders the close result of the emission wavelength while its calculated absorption

wavelength is largely deviated. Nevertheless, we find that the trend in the structural parameters (see **Table S3**) for the planarization of **PNO**, **PNS** and **PNSe** was the same, indicating that theoretical approach of PISP properties should be independent of specific functional being selected.^{39, 40} Because the computed wavelengths for absorbance by B3LYP functional are more plausibly to reproduce the onset of the experimental results, we will use the results of B3LYP functional for the following discussion.

The pertinent computational results of each transition, together with the experimental absorption and emission data in cyclohexane, are tabulated in Table 1 and Table S4 to S13. All the associated frontier orbitals of optimized ground-state geometries are depicted in Figure 4(a). Among them, the electron density distribution in HOMO are mainly localized at the N-phenyl ring, and LUMO are localized at the phenanthrene moiety, respectively. In comparison, except for PNC, the change in the electron density distribution is significant in the optimized S1 state for PNO, PNS and PNSe, in which both HOMO and LUMO are located at the dihydrodibenzo[a,c]phenazines (see **Figure 4(b)**, manifesting the π -elongation along the dihydrodibenzo[a,c]phenazine moiety. Conversely, changes of HOMO and LUMO configurations are negligible for PNC in the S_1 state (cf. S_0), being localized at the *N*-phenyl ring and the phenanthrene moiety, respectively (Figure 4(b)).



Figure 5. The structural relaxation of PNS (a) and PNSe (b) in the electronically excited state, respectively. Calculated PES scanned along the change of bending angles Θ_b from 100 to 180 ° in an increment of 10 ° for PNO in the first excited state (S₁ blue •), and ground state (S₀ red •). Open data symbol (red and blue °, °) denotes the global minimum energy in ground-state/excited-state, respectively. R* represents the initially prepared state, 1* is an intermediate with the local minimum energy in the excited state and P* denotes the final planarization state with the global minimum energy along the structural relaxation process. Notes that the structural parameters Θ_a , Θ_b and Θ_c are recorded in the figure, respectively.

The above frontier orbital analyses are fully supported by the difference in optimized geometries between ground state (S_0) and lowest lying excited state (S1). For the convenience of analysis, several structural parameters were put forward and recorded for discussion, as shown in Figures 4(c), (d) and Figure 5. For PNC, the bending angle Θ_a is calculated to be 145.58 ° and 147.99 ° in S0 and S1, respectively, which are virtually the same, supporting its lack of PISP. Regarding PNO, shown in Figure 4(d), the computational results indicate that there is only a global minimum in its S₁ state at Θ_a = 179.64 ° with $\Theta_{\rm b}$ and $\Theta_{\rm c}$ being recorded as 119.82 ° and 120.71 °. This state is denoted as P*. Hence, it is believed that upon electronic transition to R^{*}, the fast structural planarization $R^* \rightarrow P^*$ takes place for **PNO**, resulting in an increase of bending angle Θ_a , Θ_b and Θ_c , giving a $\pi\pi^*$ type of transition (emission) from the dibenzo[a,c]phenoxazine moiety.

In comparison to PNO, PNS and PNSe show distinctive properties in their computed excited-state properties. Taking PNSe as an example, shown in Figure 5(b), in addition to the R* states, PNSe was found to have two energy minima along its excited-state structure relaxation potential energy surface (PES), i.e., a local minimum at Θ_a = 128.06°, Θ_b = 113.92 ° and Θ_c = 93.94 ° representing as I*, and a global minimum state at Θ_a = 174.91°, Θ_b = 124.25 ° and Θ_c = 96.98 ° denoted as P*. Similar structural variations were obtained for PNS in toluene, shown in Figure 5(a), for which the Θ_a , Θ_b and Θ_c are recorded as 135.09°, 114.48° and 98.97 ° in its intermediate (I*) state compared with 166.98°, 123.31 ° and 102.80° in the P* state, respectively. The calculated local and global minima in the S1 state affirm the existence of the I* state and the planarized P* state, consistent with their excited-state kinetics resolved experimentally (vide supra).

To gain in-depth insights into the structural relaxation kinetics, we then performed PES simulation scanning along the bending angle Θ_a for PNO, PNS and PNSe from 100 $^\circ$ to its global minimum S_1 state, as shown in Figures 5(c), Figure S11 and Figure 5(d), respectively. Among them, PNO reveals a direct relaxation process from $R^* \rightarrow P^*$, shown in Figure 5(c), which correlates well with our photophysical results (Figure 3(b)). Clearly, in contrast, small energy barrier during the planarization process along Θ_a can be resolved in **PNS** and **PNSe**. Using PNSe as a paradigm, Figure 5(d) depicts the simulated PES for **PNSe** scanning along Θ_a for both ground state and the first excited states. In the ground state, the results indicate the global minimum geometry to be at $\Theta_a = 128.09^\circ$, named as R. Upon vertical transition of the R state, the Franck-Condon excited state R* is obtained with the computed wavelength 370 nm. As increasing the scanning angle Θ_a along S₁ PES, the local minimum was found at $\Theta_a = 128.06^\circ$, denoted as I^{*}, along the structural relaxation pathway. Further, the global minimum along Θ_a in the S₁ state was found at $\Theta_a = 180^\circ$ with 4.3 kcal/mol energy barrier at $\Theta_a = 160^\circ$. Combining these results, the vertical transition from these two excited-state minimums, i.e., I* \rightarrow I and P^{*} \rightarrow P, are calculated to be 460 and 687 nm, respectively,^{41, 42} consistent with the experimental observation (see **Figure 2(c)**). Similar results was obtained from scanning **PNS**'s PES but with a smaller energy barrier of 1.79 kcal/mol at $\Theta_a = 160^{\circ}$. The smaller barrier for **PNS** (cf. **PNSe**), in a qualitative manner, explains the faster $I^* \rightarrow P^*$ process of 4.4 ps (cf. 7.8 ps for **PNSe**)).

The above results clearly indicate that the atomic character of the substituted mono-heteroatom plays a key role for the structure-emission relationship. On the one hand, for the same family in the periodic table, the larger size of the substituted element is, the looser is the atom to attract the valence electron, resulting in the higher polarizability. This leads to more elongation of the π -conjugation upon planarization and hence the red-shifted emission, consistent with the observed λ_{em} in the order of **PNSe** > **PNS** > **PNO**. On the other hand, the larger atomic size squeezes the N-phenyl site and introduces more steric hindrance, which is evidenced by the initial bending angle Θ_{an} in the order of **PNSe** (128.09 °) < **PNS** (132.57 °) < **PNO** (143.07 °). In the case of **PNO**, the bending angle is large enough to bypass the formation of intermediate state I*, leading to a direct R* \rightarrow P* process.

2.5 Viscosity Probing

As for the potential application, recently, it becomes a strong demand for new probes reacting to the dynamic properties of their environment by concentration and polarity independent λ ratiometric response in the steady-state mode.43,44 Accordingly, the distribution of molecular dynamics variable can be achieved by processing the dual or multiple emission ratio in intensity. This requires stringent criteria in which the probe should switch between two emissive electronic states in a viscosity-dependent manner for being confident that its change is dynamic only. In view of the high activation energy for the planarization that requires a large amplitude motion, $\ensuremath{\textbf{PNSe}}$ may act as a superior molecule for sensing the viscosity free from extra stimuli such concentration, polarity and hydrogen bonding interaction. Figure 6(a) shows the ratiometric changes of the fluorescence intensity for PNSe as a function of viscosity where various cP values were prepared by mixing methanol: glycerol in different volume ratio.45 Apparently, the fit of linear plot with a steep slope of 0.027/cP (Figure 6(b)) renders both high accuracy and sensitivity in probing the surrounding viscosity. For accessing in vitro or in vivo bio-imaging, the derivation of PNSe toward water soluble derivatives is feasible and is currently in progress.



Figure 6. (a) The ratiometric changes of **PNSe** fluorescence mixed in different volume ratios of methanol and glycerol as a function of viscosity⁴⁵ at 25°C. Notes that the spectra were normalized at 470 nm. (b) The intensity ratio for the F₁ versus F₂ bands (recorded at 400 and 573 nm, respectively) as a function of viscosity shows a good linear function ($R^2 = 0.999$).

Conclusion

In summary, a series of dihydrodibenzo[*a*,*c*]phenazine derivatives with a nitrogen atom replaced by O, S, Se and CMe₂ have been strategically designed and synthesized. Combining single crystal structures and computational approaches, non-planar geometry for all title molecules were confirmed. Excited-state planarization takes place for **PNO**, **PNS** and **PNSe**, resulting in a large red-shifted emission. The emission Stokes shift in the order of **PNO** < **PNS** < **PNSe** can be rationalized by better polarization for S and Se atoms (cf. the O atom), extending π -conjugation and hence the lower energy gap after planarization. Such an elongation of π -conjugation is ruptured upon CMe₂ substitution in **PNC**, exhibiting a normal fluorescence. Femtosecond time-resolved measurements and calculated

potential energy surface unveil that **PNS** and **PNSe** undergo more pronounced PISP, in terms of emission Stokes shift, than that of **PNO**, which correlates well with the observed difference of photophysical behavior. **PNO** undergoes a $\mathbb{R}^* \rightarrow \mathbb{P}^*$ relaxation pattern whereas **PNS** and **PNSe** proceed with a sequential $\mathbb{R}^* \rightarrow$ $\mathbb{I}^* \rightarrow \mathbb{P}^*$ kinetics. For **PNO**, the bending angle is large enough to bypass the formation of intermediate state \mathbb{I}^* , leading to direct \mathbb{R}^* $\rightarrow \mathbb{P}^*$ planarization. Using **PNSe** as a prototype the feasibility of viscosity probing has been well demonstrated by the λ ratiometric response in emissive properties. The results thus demonstrate, for the first time, that the mono-hetero atom substitution fine-tunes PISP in dihydrodibenzo[*a,c*]phenazines, adding a new chapter into the control of the optically induced structural relaxation.

Experimental Section

General Synthetic Procedures. All reactions were performed under a nitrogen atmosphere using standard Schlenk techniques in flame or oven-dried glassware with magnetic stirring. External bath temperatures were used to record reaction temperatures. Ambient temperature refers to 22-26 °C. Higher than ambient reaction temperatures were maintained using oil baths, while for lower temperatures acetone/liquid nitrogen baths (-78 °C) were used. All reactions were monitored by thin-layer chromatography (TLC) and visualized by UV light (254 nm/365 nm). Toluene, dichloromethane (CH₂Cl₂) were THF were distilled over benzophenone/sodium prior to use. Commercially obtained reagents with a purity > 95 % were purchased from commercial sources (AK Scientific, Inc., Sigma-Aldrich, or Acros Organics) and used as received. Purification of reaction products were carried out by flash chromatography using Merck silica gel 60 (230-400 mesh). All yields are isolated unless otherwise specified.

Photophysical measurements. Steady-state absorption and emission spectra in solution were recorded with a Hitachi (U-3310) spectrophotometer and an Edinburgh (FS-920) fluorimeter, respectively.

For the pico-nanosecond lifetime measurements, the fundamental train of pulses from a Ti-Sapphire oscillator (82 MHz, Spectra Physics) was used to produce second harmonics (375–425 nm, 380 nm in this work) as an excitation light source. The signals were detected by a TCSPC system (Edinburgh OB 900-L), rendering a temporal resolution of ~20 ps. For the picosecond time-resolved measurement, the polarization of the pump laser was set at the magic angle (54.7 °) concerning that of the probe laser (or detecting system) to eliminate the fluorescence anisotropy.

The early dynamic study was performed by a femtosecond photoluminescence up-conversion (uPL) system pumped at 380 nm. Followed by the TCSPC measurement system, the Ti-Sapphire oscillator (82 MHz, Spectra Physics) was used to produce second harmonics (380 nm in this work) as an excitation light source to a regenerative amplifier that generated a ~ 180 fs, 1 mJ pulse (760 nm, 1 kHz). In this measurement, fluorescence from a rotating sample cell was focused in a barium borate crystal and its frequency was summed along with an interrogation gate pulse at a designated delay time with respect to the pump pulse. A half-wave plate was used to set the pump polarization at the magic angle (54.7°) with respect to the gate pulse to prevent fluorescence anisotropy contribution by solute reorientation.

Fluorescence up-conversion data were fitted to the sum of exponential functions convoluted with the instrument response function (IRF). The IRF was determined from the Raman scattering signal, and its profile was fitted to a Gaussian function with a full width at half maximum of ~220 fs.

Associated Content

Supporting Information. The supporting information is available free of charge via the Internet. Synthetic methods for the compounds, NMR, and computational details are provided.

Crystallographic data. The X-ray crystallographic coordinates for the compounds reported in this article has been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition number CCDC 1688839 (**PNO**), 1552393 (**PNS**), 1588837 (**PNSe**) and 1878212 (**PNC**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: Photoinduced structural planarization, heteroatom substitution effect, large Stokes shifted emission, mono-heteroatom substituted dihydrodibenzo[a,c]phenazines, bent heterocyclic conformation, fluorescence up-conversion

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Heteroatom substitution diversifies the photoinduced structural planarization process, giving various degrees of Stocks-shifted emission



Yi Chen, ^{‡,†,⊥} Deng-Gao Chen,^{†,⊥} Yi-An Chen,[†] Fan-Yi Meng, [†] Cheng-Ham Wu,[†] Kai-Hsin Chang, [†] Meng-Chi Chen,[†] Jia-An Lin,[†] Chun-Ying Huang,[†] Jianhua Su,[‡] He Tian, *[‡] Pi-Tai Chou,^{*,†}

Page No. – Page No.

Mono-Heteroatom Harnessing Structural Planarization for Dihydrodibenzo[*a*,*c*]phenazines