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Impact of Methoxy Substituents on Thermally Activated Delayed Fluorescence and Room-Temperature Phosphorescence in All-Organic Donor–Acceptor Systems

Jonathan S. Ward,* Roberto S. Nobuyasu,* Mark A. Fox,* Juan A. Aguilar,* David Hall,* Andrei S. Batsanov,* Zhongjie Ren,* Fernando B. Dias,* and Martin R. Bryce*‡

†Department of Chemistry and ‡Department of Physics, Durham University, Durham DH1 3LE, U.K.
§Beijing Advanced Innovation Center for Soft Matter Science and Engineering, State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology Beijing 100029, China

Study of Methoxy groups on TADF emitters

ABSTRACT: Thermally activated delayed fluorescence (TADF) and room-temperature phosphorescence (RTP) are known to occur in organic D–A–D and D–A systems where the donor group contains the phenothiazine unit and the acceptor is dibenzothiophene-S,S-dioxide. This study reports the synthesis and characterization of one new D–A and four new D–A–D systems with methoxy groups on the phenothiazine to examine their effect on emission properties in the zeonex matrix. X-ray analysis and highly specialized NMR techniques were used to characterize asymmetric methoxy-substituted derivative 3b, which is chiral at N because of an extremely high flipping barrier at the phenothiazine N atom. Based on hybrid-density functional theory computations, the methoxy substituents tune the relative stabilities of the axial conformers with respect to equatorial conformers of the phenothiazine units, depending on their substitution position. This conformational effect significantly influences both TADF and RTP contributions compared to the parent D–A–D system. It is also demonstrated that the equatorial forms of D–A–D and D–A systems in zeonex exhibit TADF. Additionally, the methoxy groups promote luminescence in D–A–D systems where only axial conformers exist. This work reveals further design opportunities for more efficient TADF and RTP molecules.

INTRODUCTION

Luminescent organic compounds are used for a wide variety of applications including security devices, organic light-emitting diodes (OLEDs), chemical sensing, and bioimaging. The tuning of emission color in conjugated organic molecules can be achieved in several different ways, such as by increasing the extent of conjugation in the system, or adding substituents to modify the electron density or the conformation within the π-system. When a molecule comprising donor (D) and acceptor (A) subunits exhibits charge-transfer (CT) emission, extension of conjugation and/or adding substituents drastically shifts the emission wavelength, thereby providing a versatile means for the rational tuning of emission color.

Thermally activated delayed fluorescence (TADF) has emerged as an efficient method for triplet harvesting via the upconversion of triplet excited states to singlet states. TADF leads to interesting fundamental photophysical properties and in particular to high-efficiency OLEDs by overcoming the 25% internal quantum efficiency limit imposed by the spin statistics of exciton formation. Although the detailed mechanism of TADF is still not fully understood, these types of molecules typically emit from a singlet charge-transfer (1CT) state, and recent experimental and computational research shows that having this state in resonance with a local triplet (3LE) state results in highly efficient reverse intersystem crossing (RISC). A fast RISC rate also results in shorter emission lifetimes because of excitons spending less time in the long-lived triplet states. Additionally, it is suggested that a short emission lifetime can result in longer device performance because of less electroluminescence quenching from charge build-up within the device. As a result, fine-tuning of the CT state is essential for the development and evaluation of new TADF molecules. The energy of the CT state in solution and in thin films can be modulated in various ways, notably by placing the emitter into different polarity solvents or solid matrices. The 1CT energy can also be shifted by the addition of substituents onto an unsubstituted D–A system.

The motivation for the present work was to explore how selective functionalization of known D–A–D and D–A molecules with methoxy groups can be used to fine-tune the emission properties, particularly in the context of TADF and room-temperature phosphorescence (RTP). The methoxy groups are in remote positions, in contrast to our previous study on the effect of methyl substituents in sterically locking positions adjacent to the D–A system. It is also demonstrated that the equatorial forms of D–A–D and D–A systems in zeonex exhibit TADF. Additionally, the methoxy groups promote luminescence in D–A–D systems where only axial conformers exist. This work reveals further design opportunities for more efficient TADF and RTP molecules.

Received: November 7, 2018
Published: March 26, 2019

Cite This: J. Org. Chem. 2019, 84, 3801–3816

DOI: 10.1021/acs.joc.8b02848
J. Org. Chem. 2019, 84, 3801–3816

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A bonds (Figure 1). For this study, phenothiazine donors in combination with dibenzothiophene-\(S,S\)-dioxide as the acceptor have recently also been investigated in phenoxazine analogs. In previous work, methoxy substituents attached at selected sites on a bis(carbazolyl)diphenylsulfone have been demonstrated to shorten emission lifetimes. This can be explained by the diastereomers in the ca. 1:1 ratio as the barrier is too high for diastereomers in the phorous solvated crystals of phenothiazine product. The isolated yield of 5 was only 10% because of difficulties in separation from a complex mixture of products. 5 was then coupled via an S_{\text{N}}Ar reaction with 2,8-difluorodibenzo thiophene-\(S,S\)-dioxide (6) to give the D–A–D compound 1c in 19% yield.

The new molecules were characterized by \(^1\)H and \(^13\)C NMR spectroscopy (General Experimental Details section and Supporting Information S1), elemental analyses, and mass spectrometry. The NMR data for 1c, 2b, and 3c revealed peaks from an averaged mixture of conformers where all conformers are freely interconverting in solutions, like their corresponding parent systems 1a, 2a, and 3a. For asymmetrically substituted phenothiazine compounds (1c and 3b), two distinct diastereomers, RR/SS or RS (meso) should be observed if the flipping at phenothiazine N is prevented. Only one set of peaks is present in the \(^1\)H NMR spectrum of 1c, indicating that diastereomers easily interconvert in solution. In contrast, for 3b, two sets of peaks were present in the NMR spectrum corresponding to two diastereomers in the ca. 1:1 ratio as the barrier is too high for inversion at nitrogen. The diastereomers in 3b could not be separated by chromatography or crystallization because of their extreme similarity; however, they were distinguished using highly specialized NMR techniques (see below).

Two independent crystallizations of 3b, from 2,2,4-trimethylpentane/THF and \(n\)-hexane/PhCl, yielded isomorphous solvated crystals of 3b-2THF and 3b-1.6PhCl with similar molecular conformations and packing motifs of the host molecules. Both structures contain two independent 3b molecules, shown in Figure 2. The dibenzothiophene (DBT) moiety is practically planar, with cis ax–ax orientation of the methoxy group on the RTP emission of these molecules with respect to 3a. This systematic study significantly contributes to our understanding of how substituents affect the multifaceted photophysics of TADF and RTP molecules.

### RESULTS AND DISCUSSION

#### Synthesis and Characterization

Detailed synthetic procedures for the compounds 1b, 1c, 2b, 3b, and 3c are reported in the General Experimental Details section. Scheme 1 shows the route to 1c as a representative example of the procedures used to prepare all the new methoxy-substituted systems. Compound 4 was synthesized via a Buchwald–Hartwig coupling of commercially available \(m\)-anisidine with 3-bromoanisole. Diarylamine 4 was then cyclized by heating with sulfur and iodine in 1,2-dichlorobenzene (DCB) to give the unusual asymmetrically substituted 2,6-dimethoxyphenothiazine product 5. The isolated yield of 5 was 10% because of difficulties in separation from a complex mixture of products. 5 was then coupled via an S_{\text{N}}Ar reaction with 2,8-difluorodibenzo thiophene-\(S,S\)-dioxide (6) to give the D–A–D compound 1c in 19% yield.

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The distribution of methoxy groups between positions i–iv is given in Table 1.

**Electrochemical Properties.** Cyclic voltammetry (CV) measurements on molecules in Figure 1 were performed in N,N-dimethylformamide (DMF) and dichloromethane (DCM) (Figures 6 and S3a–f, Tables S1 and S2). DMF is a more suitable solvent for these systems because of the wider electrochemical solvent window enabling observation of both oxidation and reduction waves. However, the oxidation waves were not reversible for 1c, 3a, 3b, and 3c in DMF. The oxidation waves in DCM were reversible for 1c, but not for 3a, 3b, and 3c even though the reverse cathodic waves are improved in DCM compared to in DMF.

Comparison of the CV traces of 1a, 1b, and 1c in Figure 6 shows that the methoxy group facilitates oxidation (by 0.12 V) at the donor group in 1b and 1c compared to 1a. A different methoxy group effect is seen in the reduction of the acceptor unit where negligible change is observed between the reduction waves of 1a and 1c, but in 1b, the reduction is more difficult with a difference of ca. 0.12 V. The differences in the reduction potentials for 1b and 1c indicate that the methoxy groups para-to the N promote electronic interactions between the donor and acceptor units more than when they are in the meta position. Inductive effects dominate when methoxy groups are in the meta-position in these systems.

The oxidation waves in 1a and 1c represent two simultaneous one-electron oxidations of both donor groups. This observation implies an absence of any electronic interaction from one oxidized phenothiazine unit on the oxidation of the second phenothiazine unit; therefore, these donors are effectively electronically isolated from each other. Nevertheless, the apparent oxidation wave in 1b in DCM is resolved into two distinct one-electron oxidation waves (Figure 7). In this case, the oxidation of one phenothiazine unit makes the second donor oxidation more difficult. The oxidized phenothiazine unit in 1b must have a higher degree of electronic conjugation with the acceptor unit for the observation of both oxidation waves. The square wave traces show a potential difference of 110 mV between the two oxidation waves, where a mixed valence cation radical of 1b is present. Two, one-electron oxidation waves are
also evident in the CV traces of 1b and 3c in DCM with approximate potential differences of 90 and 70 mV (Figure S3g).

The frontier orbital energies listed in Table 2 were estimated from CV measurements in DMF. The effect of the methoxy groups at the para positions of the parent D–A–D and D–A systems is that both HOMO and LUMO levels are higher in energies compared to the unfunctionalized derivatives.

For the tetramethyl molecules, addition of two methoxy groups (3b) does not induce a significant change in the HOMO–LUMO levels. With four methoxy groups (3c), the HOMO level increases in energy by 0.10 eV compared to 3a, but it should be noted that the oxidation waves are not reversible in DMF for these molecules (Table S1). Interestingly, the LUMO energies are not shifted by the methoxy substitutions in 3b–c. The conjugational separation between D and A in 3a–c is extensive, and as a result, even addition of methoxy groups does not alter how the DBT unit is reduced.

Computations. Hybrid density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d) level to examine which conformers are likely to be present in solutions and in zeonex. Axial (co-planar) and equatorial (perpendicular) conformations of phenothiazine are named as previously identified.50 All possible conformers of the molecules shown in Figure 1 were optimized and located as minima (Figure S4a–h). The axial conformers were the lowest energy minima in all cases. The experimental and computed geometric parameters for 1a, 3a, and 3b are in very good agreement (Table S3) which gives confidence in B3LYP/6-31G(d) as an appropriate chemistry model for D–A–D systems in the ground state. The most stable ax–eq conformer of 1a is only 1 meV higher in energy than the most stable ax–ax conformer of 1a (Figure 8). However, when methoxy groups are present, as in 1b and 1c, the ax–ax conformers are clearly preferred energetically (Table 3). Similar findings apply for the simpler D–A systems 2a and 2b, with the ax conformer being most prevalent. The calculated optimized geometries and their energies are based on gas-phase states without external effects such as intermolecular interactions present in the zeonex films. The small energy differences in the conformers may be subtly different in zeonex, and thus, the ax–eq conformer ratios for 1a–c and 2a,b in Table 3 are not considered here to be quantitative in zeonex films. The ax–ax forms are much lower in energy than the ax–eq and eq–eq for

Figure 3. (a) 600 MHz 1H NMR spectrum of 3b in DMSO-d6 and (b) pure shift 1H NMR spectrum of 3b in DMSO-d6 at 298 K. (c,d) Expansions of regions of (a,b) to show how removing multiplicity reveals the presence of multiple species. Removing the proton–proton multiplicity shows that all signals are duplicated. In many cases, equivalent peaks from the same proton in each diastereomer are <0.005 ppm apart.

Figure 4. 500 MHz 1H NMR spectra of 3b in DMSO-d6 acquired from 298 to 373 K.
3a, 3b, and 3c. Consequently, ax–ax conformers would represent at least 99% of the distribution in solution or zeonex for 3a–c at room temperature.

The rotation barriers between ax–ax and eq–ax conformers in D–A–D systems (ax and eq conformers in the case of D–A systems) were estimated by fixing the C(donor)–N(donor)–C(acceptor)–C(acceptor) torsion angle between one donor group and the acceptor moiety. Each geometry was optimized with the CNCC torsion angle as the only constraint. The torsion angle was adjusted in 5° intervals to give relative rotation energy profiles (Figure S4i–k). The rotation barrier is only 0.12 eV for 1a, suggesting that ax–ax and eq–ax conformers interconvert in solution at room temperature along with many other conformers. On fabrication of a solid zeonex film with evaporation of the solvent, the conformers are locked in the zeonex matrix, and interconversion is negligible in the solid matrix as significant geometrical distortions would have to occur for conformers to interconvert (e.g., ax–ax to ax–eq).

By constraining the "NC4S" ring to be planar and optimizing the geometries, the inversion barriers at nitrogen were estimated. For 1a, 1b, 1c, 2a, and 2b, the inversion barrier energies are similar to the low rotation barrier energies. As a result, these conformers, including diastereomers, interconvert

Figure 5. High-resolution pure shift 1H–13C HSQC NMR spectrum of 3b produced combining compressive and covariance techniques.

Figure 6. Cyclic voltammograms of 1a, 1b, and 1c in 0.1 M TBAPF6 in DMF.

Figure 7. (a) CV and (b) square wave voltammetry (SWV) traces for 1b in DMF.

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<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>HLG (eV)</th>
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<td>3c</td>
<td>−5.81</td>
<td>−2.70</td>
<td>3.11</td>
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in solutions at room temperature. The $^1H$ peaks observed in the NMR spectra of these compounds (Section S1) are sharp for each environment, suggesting that the peaks are averaged because of rapid interconversions of many different conformers in solutions. For 3a, 3b, and 3c, the rotation barrier energies are 0.29, 0.32, and 0.33 eV, respectively, which mean that no inversion barrier energies are much higher in 3a, 3b, and 3c at 1.26, 1.31, and 1.35 eV, respectively. Such values indicate that no inversions take place at room temperature, thus stereoisomers would not interconvert. Because there are distinct diastereoisomers, (RR/SS) and meso, in 3b, separated peaks corresponding to these isomers are observed in the solution-state NMR spectra of 3b (Figures 3–5 and S2). All these studies together highlight the rigidity of molecules 3a–c, and this suggests why the excited states can emit at such long lifetimes (ms timescale; see below).

The LUMO and HOMO energies obtained from electronic structure calculations on the two static “gas-phase” minima of 1a, with essentially identical energies at B3LYP/6-31G(d) level, show notable differences between ax–ax and ax–eq conformers of –0.41 and +0.37 eV for LUMO and HOMO, respectively (Figure 8). By contrast, the frontier orbital energies differ by only +0.17 eV for the LUMO and +0.20 eV for the HOMO from 3a to 3c with methoxy groups (Table 3). The conformations in these D–A–D and D–A systems therefore influence the frontier orbital energies, in addition to the electronic effects of the methoxy groups.

The frontier orbitals of 1b and 1c with different methoxy substituent positions were examined in detail in order to explain the differing CV data. There are increased orbital contributions from the acceptor unit to the LUMO and HOMO of 1b compared to 1c (Figure 9). This supports the increased electronic conjugation between the donor and acceptor units in 1b resulting in the observation of a mixed valence radical cation in the CV data of 1b (Figure 7).

The computations demonstrate how several different ax–ax and ax–eq conformers exist in solutions for 1a, 1b, and 1c and different ax and eq conformers are present in 2a and 2b. The ax–ax conformers are essentially the only conformers present in 3a, 3b, and 3c solutions. Detailed emission measurements were performed on these systems in zeonex in order to identify the different emissions and their percentage contributions arising from axial and equatorial conformers.

**Photophysical Properties.** Absorption spectra in dichloromethane solution showed very similar profiles for 1b, 2b, 3b, and 3c, but a different profile was observed for 1c with a more intense band at 260 nm (Figure S5a). This difference is attributed to the methoxy groups at meta-positions to N for 1c, in contrast to para for the other molecules. The lowest energy band cut-offs are at 410 nm for 1b and 1c, 400 nm for 2b, and 385 nm for 3b and 3c. This trend suggests that the highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gap (HLG) energy increases in

![Figure 8. Most stable ax–ax and eq–ax conformers of 1a with frontier orbital energies from DFT calculations at the B3LYP/6-31G(d) level.](image)

![Figure 9. Frontier orbital energies of the lowest energy minima of 1b and 1c calculated at the B3LYP/6-31G(d) level. The percentages represent the orbital contribution of the acceptor unit (dibenzothiophene-5,5-dioxide) to the frontier orbitals.](image)

<table>
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<th>Table 3. Computed Energies in eV at B3LYP/6-31G(d)</th>
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<tr>
<td><strong>energy difference</strong></td>
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<td>1a</td>
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The energy difference between the lowest energy axial and equatorial conformers. For 1a–1c and 3a–3c, ax–ax vs ax–eq. For 2a and 2b, ax vs eq.

The relative ratio of axial and equatorial conformers in solution at 290 K, assuming that only two conformers are present. The rotation barrier energy about the N–C bond between donor and acceptor units. The inversion barrier energy at one nitrogen atom. For lowest energy axial conformers only.

DOI: 10.1021/acs.joc.8b02848
J. Org. Chem. 2019, 84, 3801–3816
the sequence $1b/1c < 2b < 3b/3c$. Photophysical measurements on the five methoxy-substituted molecules allow comparison with the reported emission data of the parent D–A–D and D–A structures $1a$, $2a$, and $3a$ to probe structure/property relationships for achieving TADF or RTP, or both. Figure 10

![Normalized Intensity vs Wavelength](image)

**Figure 10.** Steady-state emission spectra of $1a$, $1b$, and $1c$ in the zeonex matrix at 290 K in the absence of oxygen. The onset of the main emission band is shown with corresponding energy for the 0–0 transition. The 0–0 transition allows accurate comparison of the emission.

shows the steady-state emission spectra of $1a$–$c$ in the zeonex matrix in the absence of oxygen: the emission bands of $1b$ and $1c$ broaden and red-shift with respect to $1a$. The order of emission maximum energies is $1b < 1c < 1a$ which does not agree with the order of estimated HLG energies from CV measurements ($1c < 1a < 1b$; Table 2). Several different emissions must be present that complicate interpretations of these spectra. This is not surprising as many different static conformers in varying ratios would be present in zeonex. Unlike $1a$, the steady-state spectra of both $1b$ and $1c$ show high energy band shoulders where the shoulder is much more pronounced in $1b$ than in $1c$. These shoulders may be attributed to local fluorescence ($1LE$), but may contain some contributions from CT fluorescence from the axial conformer $1CT(ax)$. Phosphorescence spectra for $1b$ and $1c$ at 80 K in zeonex show poorly structured bands with similar high energy onsets at 2.71 and 2.74 eV, respectively (Figure S5b).

The larger effect of the methoxy groups at para positions, over the e

ratio of 6.50 in the zeonex matrix, whereas $1b$ and $1c$ have lower ratios of 1.66 and 2.52, respectively. The data for methoxy-substituted $1b$–$c$ compared with $1a$ (no methoxy groups) indicate that the methoxy groups decrease the contribution of triplet excited states to the emission. DF and phosphorescence are dependent on oxygen as triplet excited states are involved in these emission pathways. A similar trend is observed with the D–A series, where the $I_{no O2}/I_{O2}$ ratio drops from 5.09 in $2a$ to 2.04 in $2b$. Both $2a$ and $2b$ show high energy shoulders which can be attributed to fluorescence from the local singlet state ($1LE$).

The effect of methoxy groups on the $I_{no O2}/I_{O2}$ intensity ratios is quite different for the tetramethyl derivatives, with values of 2.25, 8.69, and 2.31 for $3a$, $3b$, and $3c$, respectively. The emission spectra for $3a$–$c$ are clearly different from other D–A–D and D–A systems here, with well-structured emission in the absence of oxygen. Subtractions of the emission spectra of $3a$–$c$ in the absence of oxygen (black lines in Figure 11) give the emission spectra of $3a$–$c$ from the triplet states only (Figure 12 left panel). The virtually identical structured emission spectra of $3a$–$c$ in Figure 12 (left panel) are identified as RTP, presumably from combinations of local donor and acceptor contributions. The phosphorescence spectra in Figure 12 generated from subtractions match very closely with the ms delay time-jump data for $3b$–$3c$ (Figure S5e).

These data highlight how deconvolution can be effectively utilized to identify overlapping emissions bands. Closer inspection of the oxygen-independent emission spectra for $3a$–$c$ reveals differences where the structured high energy band for $3c$ is at considerably lower energy than the corresponding band for $3a$ or $3b$ (Figure 12 right panel). Such a shift indicates the effect of the four methoxy groups in $3c$. In the series $3a$–$c$, the conjugational separation between donor and acceptor units is extensive. Four methoxy groups are required to induce a red shift in the emission of $3c$. The data suggest that two methoxy groups in $3b$ are insufficient for significant donor–acceptor communication and a red shift is not observed.

The structured high energy band is not dependent on oxygen and is therefore assigned as local fluorescence ($1LE$). Broad lower-energy fluorescence bands are also present in these tetramethyl systems, which are assigned as CT fluorescence ($1CT(ax)$) from axial conformers. The assignments of $1LE$ and $1CT(ax)$ emission peaks are based on the fact that $1LE$ emission appears at much higher energy, and has fine structure unlike the broad $CT(ax)$ emissions. The CT emission peaks are at wavelengths $>500$ nm, whereas the $1LE$ emission peaks are below $450$ nm. Therefore, the $1LE$ emission is clearly distinguished from the other emissions despite some overlap of the spectra. The sequential increase in the PLQY from $3a$ (7%) to $3b$ (13%) to $3c$ (17%) can be attributed to an increase of the local phosphorescence induced by the two methoxy groups in $3b$, and to an increase in the fluorescence intensity due to the effect of the four methoxy groups in $3c$. PLQY measurements are summarized in Figure S5f, highlighting the effect of the methoxy groups in the different positions in these systems. Curiously, methoxy groups in the meta-positions on $1c$ do not reduce the PLQY of the D–A–D system compared to $1a$.

Time-dependent emission measurements reveal DF emissions for $1b$, $1c$, and $2b$ by comparison with data previously reported for $1a$ and $2a$ (Figure 13). The time period of
around 1 μs between the occurrence of prompt fluorescence (PF) (≈10 ns) and phosphorescence (Ph) (≈1 ms) corresponds to the decay of DF. The DF spectra are shown for 1b and 1c in Figure S5b. Variable-temperature time-dependent plots confirm that 1a, 1b, and 1c have delayed emission components in the 125 ns to 0.1 ms range where these molecules emit via a TADF pathway (Figure S5c,d). No significant increase in the delayed emission intensity for molecule 1c is observed by raising the temperature above 180 K, compared to 250 K for 1a, with clear increases observed up to 320 K for 1b. The variable-temperature and time-dependent
plots for 2a and 2b also show TADF emission in the 150 ns to 3 ms range.

Prompt fluorescence (PF) results from the direct decay of the singlet state [1LE or 1CT(eq) or 1CT(ax)]. Only the equatorial conformation of the studied molecules exhibits RISC. Only CT(eq) emission is observed in the DF in the microsecond region, with the exception of the slow CT(ax) emission from 3c due to conformational separation.

In molecules 1a–c and 2a–b, a mixed conformational distribution is observed (Table 3); however, no CT(ax) emission for 1a–c, 2a–b is observed. Literature reports show that phenothiazine derivatives that are exclusively in the ax–ax (>90%) conformation show a significantly blue-shifted CT band. Only 1CT(eq) emission is observed for molecules 1a–c and 2a–b as the CT(eq) emission in the μs delayed region matches very closely with the CT emission observed in the steady-state spectra. Any blue shift observed in the steady-state emission spectra of 1a–c and 2a–b in the absence of oxygen (Figure 11) has been clearly assigned to phosphorescence using the time-dependent emission and time-jump data (Figure S5b,d). In complete contrast, for 3a–c, the molecules are 100% in the axial conformation. Because of the high rigidity of 3a–c (as shown by the rotational and flipping barriers in Table 3), the axial–axial conformation becomes more emissive compared to the same conformation in 1a–c and 2a–b.

Time-dependent emission plots for 3a and 3b reveal no emissions in the range of 0.1 μs and 0.2 ms between PF and RTP.
This happens in general for signals that decay at a very slow rate. The $^1\text{LE}$ and $^1\text{CT}$(ax) emissions in 3a–b have completely decayed before the early microsecond region as they have fast decay rates. The phosphorescence emission decays at an extremely slow rate, and so no photons are detected in the microsecond region where the integration times used are still reasonably short. Therefore, a time gap with no emission is observed, even with a highly sensitive ICCD camera. This implies no DF emissions from these compounds in zeonex. Remarkably for 3c, the time range where no emissions were observed is much smaller, between 6 µs and 0.2 ms. There is emission with slow times in the range of 0.1–6 µs. This µs emission from 3c is extremely weak, and it is detected by the sensitive ICCD camera. The emission from 3c at µs times is so weak (<0.1% of the total emission) that this minor feature was not pursued any further. Such µs emissions are not detected in 3a–b.

From all the emission spectra (oxygen, deoxygenated, and time-dependent) with spectral subtractions, the different emissions in the TADF molecules 1a, 1b, 1c, 2a, and 2b are assigned as shown in Figure 14. In the $^1\text{CT}$(eq) (CT fluorescence from the equatorial conformer) transitions, the intensity of TADF (DF) with respect to PF decreases in the order

\[
1a > 1c > 1b.
\]

It is interesting that the decrease of the RTP intensity is in the order 1a to 1c then 1b and is coupled with the increase of the local fluorescence intensity. In 1a–c, the methoxy groups facilitate local fluorescence at the expense of RTP due to increased ax–ax emission contributions.

The situation is different with the D–A system 2a which appears to exhibit intense TADF and little, if any, RTP in steady-state emissions (Figure 14). The time-dependent emission plot for 2a suggests some weak RTP between 10 and 1 ms (Figure 13). While it is difficult to confirm any significant RTP within the $^1\text{CT}$ band in 2a, the emission does not show any blue shift in the absence of oxygen (Figure 11). This is in contrast to 1a, where the emission significantly blue-shifts in the absence of oxygen because of the higher energy local phosphorescence. The D–A system 2b exhibits a similar blue shift without oxygen as in 1a and this is also attributed to RTP. The phosphorescence spectrum of 2b generated by deconvolution matches very closely with the time-jump data (Figure S5d). Therefore, it is suggested that the methoxy groups promote RTP with respect to the parent system 2a. All of the information from the emission data is summarized in Table 4.

Table 4 summarizes the effect of the methoxy groups on the emission of the molecules studied herein. The key points are as follows: (i) methoxy groups red-shift the emission in 1b–c and 2b with respect to the parent systems 1a–2a. (ii) The para-methoxy groups lower the PLQY of 1b and 2b, but PLQY remains essentially the same when meta-methoxy substituents are used (1c). (iii) The methoxy substituents in 1b–c and 2b widen the $\Delta E_{\text{ST(eq)}}$ gap as a result of the red shift in the $^1\text{CT}$ energy where the triplet energy remains effectively unchanged. The widening of the $\Delta E_{\text{ST(eq)}}$ gap in combination with the increased axial contributions explains why 1b–c and 2b have reduced TADF contributions. (iv) It is, however, interesting that the PLQY is not reduced in 1c, suggesting that meta-methoxy substitution could be useful in future TADF analogs for fine tuning $\Delta E_{\text{ST}}$. (v) In 3a–c, the methoxy groups do not significantly shift the phosphorescence emission but appear to promote RTP contributions and also raise the PLQY. These factors are all important for designing future TADF and RTP analogs. Combining all the data presented in this manuscript, the barrier for the interconversion of conformers is expected to be very high in the solid state. There is strong evidence for this in the spectra of 1a, 1c, and 2b where the ax–ax conformer clearly exists in the zeonex films. For these molecules, RTP is seen at long times (into the ms region, see Figure 13). For the molecules studied, the axial–axial conformation is required to observe RTP, as in the other conformations (ax–eq) and (eq–eq), RTP is not seen because of fast ns or early µs scale relaxation processes (CT emission and TADF). Observing RTP in these molecules on the ms timescale strongly suggests the ax–ax conformation cannot convert when locked in the rigid zeonex matrix as interconversion would result in fast CT emission instead. The gas phase calculations are performed in the ground state as the conformational distribution in the solid state is expected to be the average distribution in solution.

![Jablonski diagrams to represent the photophysical processes that occur in (a) TADF materials (molecules 1a–c, 2a–b) and (b) for phosphorescent (Ph) materials (molecules 3a–c).](image-url)
Methoxy groups at sites remote from the D–A bonds have been shown to modulate the emission properties of a systematic series of D–A–D and D–A organic molecules in a sophisticated fashion through a balance of electronic and conformational effects. The energetic preference for axial over equatorial conformers of the phenothiazine units upon addition of methoxy groups has been established by hybrid-DFT calculations broadly follow the trends observed experimentally and support the assignments given.

### CONCLUSIONS

Methoxy groups at sites remote from the D–A bonds have been shown to modulate the emission properties of a systematic series of D–A–D and D–A organic molecules in a sophisticated fashion through a balance of electronic and conformational effects. The energetic preference for axial over equatorial conformers of the phenothiazine units upon addition of methoxy groups has been established by hybrid-DFT calculations broadly follow the trends observed experimentally and support the assignments given.

### GENERAL EXPERIMENTAL DETAILS

All reactions were carried out under an argon atmosphere unless otherwise stated. Starting materials were purchased commercially and were used as received. Solvents were dried using an Innovative Technology solvent purification system and were stored in ampoules under argon, with the exception of anhydrous DCB, which was purchased from Sigma-Aldrich and used as received.

Thin-layer chromatography (TLC) analysis was carried out using Merck silica gel 60 F254 TLC plates and spots were visualized using a TLC lamp emitting at 365, 312, or 254 nm. Silica gel column chromatography was performed using silica gel 60 purchased from Flurochem.

Melt points were determined in an Exeter Analytical E-440 machine.

Any stated use of hexane refers to a mix isomers grade with the exception of crystal growth for X-ray crystallography, where the methoxy group orientations are different decays/overlapping transitions that cannot be accurately fitted. For this reason, assignment of emission peaks is given at positions/ranges in time rather than as fitted decays. For initial development of these methods; see a previously published literature study. PLQY measurements were performed using a Quantaurus-QY Absolute PL quantum yield spectrometer using zeonex films prepared as described above.

X-ray Crystallography. Crystals of X-ray quality were obtained by layering n-hexane or 2,2,4-trimethylpentane on top of a solution of 3b in THF or PhCl, which gave isomorphous solvates. Diffraction experiments were carried out on a D8 Venture 3-circle diffractometer (Bruker AXS) with a PHOTON 100 CMOS area detector, using Cu Kα.
radiation (λ = 1.54184 Å) from an Incoatec 1s microsource with a focussing mirror and a Cryostream (Oxford Cryosystems) open-flow 8 N2 gas cryostat. The intensities were corrected for absorption by numerical integration based on crystal face-indexing, using SADABS program.63 The structures were solved by dual-space intrinsic phasing method using the SHELXT 2018/2 program and refined by full-matrix least squares using SHELXL 2018/3 software65 on the OLEX2 platform.66 Crystal data are reported in Table S4 in Supporting Information. The asymmetric unit of 3b-2THF contains two molecules of 3b, one ordered THF molecule, two disordered THF molecules which could not be refined satisfactorily and were masked using the PLATON SQUEEZE program,67 and some part-occupied THF positions statistically mixed with part-occupied methoxy groups, tentatively estimated as adding up to one more THF molecule per asymmetric unit. The asymmetric unit of 3b-1.6PhCl contains two molecules of 3b, one ordered and two disordered chlorobenzene molecules in general positions, and 20% of a chlorobenzene molecule disordered around an inversion center.

CIF files have been deposited with the Cambridge Structural Database: CCDC-1866643 (3b-2THF) and 1866636 (3b-1.6PhCl).

Synthesis and Characterization. 2,8-Bis(3,7-dimethoxyphenothiazin-10-yl)-dibenzo[b,f]thiophene-5,5′-dioxide (1b). To a stirred solution of 3,7-dimethoxyphenothiazine (100) (300 mg, 1.16 mmol, 2 equiv) in dry DMF (10 mL) under argon was added Cs2CO3 (0.94 g, 2.89 mmol, 5 equiv). The reaction mixture was stirred at ambient temperature over 30 min after which 2,8-dibromodibenzothiophene-5,5′-dioxide (6) (146 mg, 0.58 mmol, 1 equiv) was added in one portion. The reaction mixture was then heated with vigorous stirring at 155 °C for 16 h. The reaction mixture was allowed to cool to ambient temperature, and then water (50 mL) was added. The aqueous mixture was then extracted with EtOAc (3 × 50 mL). The combined organic extracts were washed with 1 M HCl(aq) (2 × 100 mL), dried with MgSO4 and filtered. The solvent was removed under reduced pressure to give an orange solid which was recrystallized from boiling hexane with dropwise addition of ethanol until dissolution was achieved. Cooling to −18°C resulted in product crystallization. The crystals were collected by filtration and washed with cold hexane to give the title product as a dark yellow solid (50 mg, 12%).

1H NMR (400 MHz, DMSO-d6): δ 7.65 (d, J = 8.7 Hz, 2H), 7.52 (d, J = 8.8 Hz, 4H), 7.21 (d, J = 2.8 Hz, 4H), 7.02 (dd, J = 8.8, 2.8 Hz, 4H), 6.92 (d, J = 2.3 Hz, 2H), 6.85 (dd, J = 8.7, 2.3 Hz, 2H), 3.85 (s, 12H);13C{1H} NMR (151 MHz, DCl3): δ 159.9, 156.8, 149.6, 143.0, 142.4, 133.9, 133.1, 129.3, 127.6, 123.7, 122.7, 120.3, 118.9, 116.5, 113.4, 111.2, 110.2, 107.6, 56.0; HRMS-ASAP-TOF+ m/z: calcd for C40H30N2O6S3·[M + H]+: 731.1339; found: 731.1331; Anal. Calcld for C40H30N2O6S3·[M + H]+: C, 65.74; H, 4.14; N, 3.83; mp deg. >350 °C.

2-(3,7-Dimethoxyphenothiazin-10-yl)dibenzo[b,f]thiophene-5,5′-dioxide (2b). 2-Bromodibenzothiophene-5,5′-dioxide (13) (590 mg, 2.2 mmol, 1 equiv) and 7.5 mmol, 1.5 equiv) was added and the mixture was heated at 100 °C with stirring under argon for 18 h. After cooling to ambient temperature, water (150 mL) was added and the organic products were extracted into CH2Cl2 and washed with water and brine. The organic layer was dried over MgSO4 and the solvent was removed under vacuum to give the crude product. The crude product was purified by silica gel column chromatography eluting with 50% CH2Cl2/petroleum ether (v/v). Removal of the solvent under reduced pressure gave a crude solid which was recrystallized from acetone to give a pure product as a white solid (240 mg, 25% yield).

To a stirred solution of 101 (100 mg, 0.34 mmol, 0.1 equiv) were added K2CO3 (0.28 g, 2.0 mmol, 5 equiv) and 2,8-dibromodibenzothiophene-5,5′-dioxide (6) (390 mg, 1.6 mmol, 1 equiv) was added under a high flow of argon, and the mixture was heated to 110 °C for 18 h. The mixture was cooled to ambient temperature, water (150 mL) was added and the organic products were extracted into CH2Cl2 and washed with water and brine. The organic layer was dried over MgSO4 and the solvent was removed under vacuum to give the crude product. The crude product was purified by silica gel column chromatography eluting with 50% CH2Cl2/petroleum ether (v/v). Removal of the solvent under reduced pressure gave a crude solid which was recrystallized from acetone to give a pure product as a white solid (240 mg, 25% yield).
solid. Recrystallization in boiling hexane with the dropwise addition of crude oil. The crude oil was purified with stirring for 18 h. On cooling the reaction mixture to ambient temperature, water (25 mL) was added, and the aqueous layer was extracted using EtOAc (4 × 50 mL). The organic layers were combined, washed with 1 M HCl (2 × 50 mL), separated, dried with MgSO4, filtered, and washed with cold Et2O to give the product as a white solid (87 mg, 26%).

2H NMR (400 MHz, CDCl3): δ 7.42 (d, J = 9.2 Hz, 2H), 6.93 (d, J = 2.5 Hz, 4H), 6.85 (d, J = 2.5 Hz, 4H), 6.38–6.43 (m, 4H), 3.86 (s, 12H), 2.36 (s, 12H). 13C{1H} NMR (176 MHz, CDCl3): δ 158.3, 151.0, 138.2, 137.9, 133.56, 129.4, 122.9, 115.6, 114.4, 111.3, 105.3, 56.0, 18.4; HRMS-ASAP-TOF m/z: calcld for C8H8N2O3S (M + H)+, 258.1489; found, 258.1485.

Using general procedure B, bis-(2-methyl-4-methoxyphenyl)amine (4.65 g, 33.90 mmol, 1.13 equiv), NaOBU (5.77 g, 60.00 mmol, 2 equiv), Pd(dppf)Cl2.CH2Cl2 (0.74 g, 0.90 mmol, 0.03 equiv), toluene (100 mL), and 4-bromoanisole (6.04 g/4.24 mL, 30 mmol, 1 equiv) were used to make the title compound with heating at 100 °C for 4 h. The crude mixture was extracted as described for 4-methoxy-2-methyl-N-(toly)lanilin (7). Column chromatography was performed as detailed in general procedure A. Removal of solvent under reduced pressure gave the title compound as a red solid (5.08 g, 74%).

Using general procedure A, 4-methoxy-2-methyl-aniline (4.65 g, 33.90 mmol, 1.13 equiv), NaOBU (5.77 g, 60.00 mmol, 2 equiv), Pd(dppf)Cl2.CH2Cl2 (0.74 g, 0.90 mmol, 0.03 equiv), toluene (100 mL), and 4-bromoanisole (6.04 g/4.24 mL, 30 mmol, 1 equiv) were used to make the title compound with heating at 100 °C for 4 h. The mixture was extracted as described for 4-methoxy-2-methyl-N-(toly)lanilin (7). Column chromatography was performed as detailed in general procedure A. Removal of solvent under reduced pressure gave the title compound as a red solid (5.08 g, 74%).

Using general procedure A, 4-methoxy-2-methyl-aniline (4.65 g, 33.90 mmol, 1.13 equiv), NaOBU (5.77 g, 60.00 mmol, 2 equiv), Pd(dppf)Cl2.CH2Cl2 (0.74 g, 0.90 mmol, 0.03 equiv), toluene (100 mL), and 4-bromoanisole (6.04 g/4.24 mL, 30 mmol, 1 equiv) were used to make the title compound with heating at 100 °C for 4 h. The mixture was extracted as described for 4-methoxy-2-methyl-N-(toly)lanilin (7). Column chromatography was performed as detailed in general procedure A. Removal of solvent under reduced pressure gave the title compound as a red solid (5.08 g, 74%).
(420 mg, 1.66 mmol, 0.18 equiv), and DCB (12 mL) were used to make the title compound. The compound was purified by silica gel column chromatography initially eluting with hexane, followed by EtOAc/hexane 5:50 (v/v) increasing in 5% increments. The column was repeated because of difficulties recovering DCB in the first column. Removal of the solvent under reduced pressure gave the product as a yellow solid (405 mg, 17%).

3H NMR (400 MHz, acetone-\(d_6\)): \(\delta\) 7.41 (s, 1H), 6.68–6.62 (m, 2H), 6.62–6.56 (m, 4H), 3.70 (s, 6H).

1,9-Dimethyl-3-methoxyphenothiazine (11). Using general procedure B, 4-methoxy-2-methyl-N-(\(\alpha\)-tolyl)alanine (7) (3.50 g, 15.4 mmol, 1 equiv), sulfur (1.48 g, 46.2 mmol, 3 equiv), I\(_2\) (0.51 g, 2.0 mmol, 0.13 equiv), and DCB (20 mL) were used to make the title compound. The compound was purified by silica gel column chromatography initially eluting with hexane, followed by EtOAc/hexane 5:30% (v/v) increasing in 5% increments. Removal of solvent gave a yellow solid (1.63 g, 41%).

1H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.92 (d, \(J\) = 7.4 Hz, 1H), 6.87 (d, \(J\) = 7.4 Hz, 1H), 6.79–6.71 (m, 1H), 6.51 (s, 1H), 6.48 (d, \(J\) = 2.7 Hz, 1H), 5.69 (s, 1H), 3.70 (s, 3H), 2.24 (s, 3H), 2.23 (s, 3H); \(^{13}\)C NMR (101 MHz, acetone-\(d_6\)): \(\delta\) 156.1, 141.8, 134.6, 129.8, 125.1, 124.5, 123.2, 122.5, 120.3, 118.6, 115.7, 110.3, 55.8, 17.2, 17.0; HRMS-ASAP-TOF+ m/z: calcld for C\(_{16}\)H\(_{18}\)NO\(_2\)S [M+H]+, 288.1054; found, 288.1052; mp decomp. 179°C.


**REFERENCES**


