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Tunable Luminescence of Bithiophene-Based Flexible Lewis Pairs

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S *Supporting Information*

ABSTRACT: Bithiophene-based flexible Lewis pairs with $P(O)R_2$ (R = phenyl, isopropyl) and $BMes_2$ (Mes = 2,4,6-trimethylphenyl) functionalities are able to toggle between closed, Lewis adduct and open, unbound Lewis pair structures. The open structure is favored in strong hydrogen bond donating solvents or at higher temperatures giving rise to an intense charge-transfer (CT) luminescence, while the closed structure without this emission dominates in non-hydrogen bond donating solvents or at lower temperatures. Intermediate solvents result in an equilibrium mixture of both structures, which shows unusual mixed emission that is dependent on excitation wavelength.

Lewis acids and bases are important reactive species with applications in catalytic transformations,[1] molecular recognition, and chemical sensing.[2] Molecules containing both Lewis acid and base functionalities (Lewis pairs) are intriguing systems where either Lewis adducts or sterically hindered, unbound species with unusual reactivity, such as frustrated Lewis pairs (FLPs), can form.[3] Although most Lewis pairs exist either as unreactive adducts or reactive unbound pairs, the development of systems where these forms exist in equilibrium with each other is intriguing.[4] Such "flexible" systems may allow control of chemical behavior by tuning of the solvent, temperature, or other environmental factors to favor either the unbound form or Lewis adduct. The ability to use absorption or emission color to instantaneously assess the state of such flexible systems would be useful, yet the photophysical properties of unbound Lewis pairs have rarely been explored to date.[5] It is known that the presence of charge-accepting Lewis acidic boron centers gives rise to intense light absorbance or photoluminescence,[6] which is absent when 4-coordinate boron is formed upon reaction with fluoride or cyanide anions.[2a,d] Carefully designed flexible Lewis pairs may therefore enable reversible tuning of photophysical behavior, based on whether the boron is free or engaged in a Lewis adduct. Absorption or emission changes can then be used to conveniently assess catalytic activity in situ and may allow applications in sensors.

Herein we report a flexible boron-phosphine oxide Lewis pair system in which manipulation of the equilibrium between unbound pair and Lewis adducts results in a fundamental alteration in the photophysical properties of the system. A key feature of this system is the flexibility of the bithiophene backbone, which allows rotation about the interannular C−C bond to form the closed structure as a Lewis adduct or the open structure as an unbound Lewis pair (Scheme 1). The phosphine
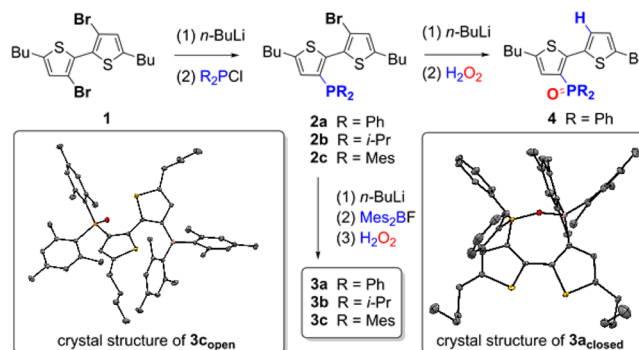
Scheme 1

R = Ph 3a$_{open}$
R = i-Pr 3b$_{open}$

R = Ph 3a$_{closed}$
R = i-Pr 3b$_{closed}$
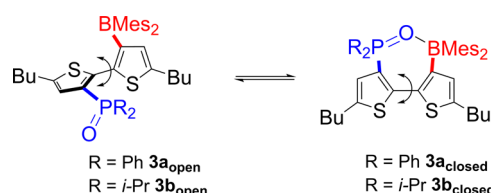
oxide functionality as the Lewis basic component of the system has special advantages in that it is air stable, is easy to synthesize, and has dual functionality as both Lewis base[7] and strong hydrogen bond acceptor (HBA) capable of forming hydrogen bonds (HBs) with amines,[8] alcohols,[9] H_2O, and H_2O_2,[10] and even weak hydrogen bond donors such as $CHCl_3$.[11] Other intramolecular borane-phosphine oxide pairs are known; however, none of them are able to switch between three and four coordinated boron centers.[4i,12]

The boron-phosphine oxide (B-PO) Lewis pairs **3a−3c** were obtained from 3,3′-dibromo-5,5′-dibutylbithiophene **1** by sequentially introducing the phosphine and Lewis acidic boron centers (Scheme 2). Oxidation gave air-stable **3a−3c** as light yellow solids. Compound **4**, without the boron center, was synthesized in a similar fashion for comparison.

The solid-state structure of **3a** (Scheme 2, right inset) obtained by crystallizing the compound in acetone shows that the phosphine oxide moiety forms a Lewis adduct with the boron center (**3a$_{closed}$**), despite the presence of the bulky mesityl

Scheme 2[a]

1

(1) n-BuLi
(2) R_2PCl

2a R = Ph
2b R = i-Pr
2c R = Mes

(1) n-BuLi
(2) H_2O_2

4 R = Ph

(1) n-BuLi
(2) Mes_2BF
(3) H_2O_2

3a R = Ph
3b R = i-Pr
3c R = Mes

crystal structure of 3c$_{open}$

crystal structure of 3a$_{closed}$

[a]Inset: ORTEP diagrams of **3c$_{open}$** and **3a$_{closed}$** with 50% thermal ellipsoids (hydrogen atoms are not shown).

groups. The B–PO interaction of **3a_closed** is comparable to that in a related Lewis adduct supported on a 1,8-naphthalene linker;[13] however, in that case the structure is highly congested and rigid, whereas in **3a_closed** there is sufficient flexibility for repulsions to be minimized. In **3a_closed** the two thiophene rings are slightly twisted relative to each other with a small S–C–C–S dihedral angle of 20.94(15)°, in agreement with the DFT calculated angle for this structure (see below). The P–O bond length in **3a_closed** (1.5194(10) Å) is longer than that in a similar, but free, phosphine oxide[7] due to weakened oxygen-to-phosphorus bonding. The infrared (IR) spectrum of **3a** in the solid state (Figure S1a) shows a P=O stretching band ($\nu_{P=O}$) at 1116 cm^{-1}, close to values obtained for similar Lewis adducts,[14] and consistent with the bonding found in the crystal structure. By contrast, **3c** crystallizes as an unbound Lewis pair **3c_open** (Scheme 2, left inset) due to substantial steric hindrance in this compound. In **3c_open** the S–C–C–S dihedral angle is large (130.10(7)°), and the P=O bond length (1.4846(8) Å) and IR stretching band ($\nu_{P=O}$ = 1185 cm^{-1}) are both typical of free phosphine oxides.

The solution structure of compound **3a** was found to vary with solvent, as evidenced by both IR and NMR spectra. In hexanes, a non-HB donating solvent, the P=O stretching band is at 1120 cm^{-1} (Figure S1b), similar to $\nu_{P=O}$ in the solid state and consistent with a Lewis adduct (**3a_closed**) also being present in this solvent. In addition, the ^{31}P{^{1}H} NMR spectrum in hexanes shows a single peak at δ = 34.5 ppm, significantly downfield from the peak in MeOH-d_4 or CDCl$_3$ (Figure 1a) and broadened
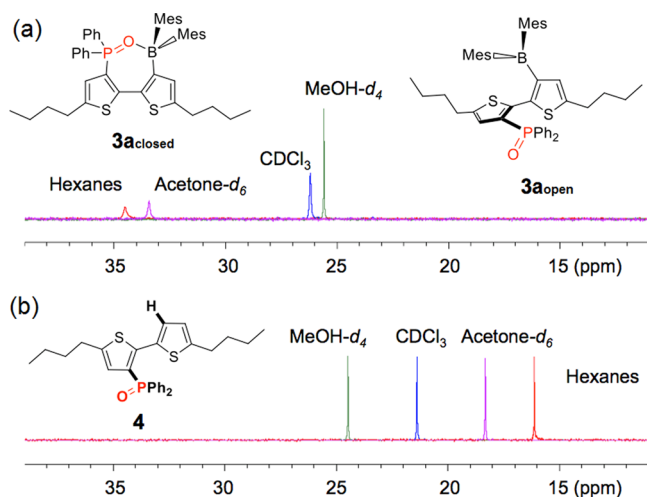

Figure 1. Stacked ^{31}P{^{1}H} NMR spectra of (a) **3a** and (b) **4** in various solvents.

(peak width = 28.5 Hz) relative to the narrower peak in MeOH-d_4 (peak width = 28.5 Hz). These spectral features are consistent with the Lewis adduct **3a_closed** being present in hexanes, with the broadening attributed to the presence of the quadrupolar ^{10}B and ^{11}B centers bonded to the oxygen center.

In the strong HB solvent MeOH, $\nu_{P=O}$ of **3a** is at 1187 cm^{-1} (Figure S1c), similar to the value typically observed for free P=O bonds.[15] The sharp upfield resonance in the ^{31}P{^{1}H} NMR in MeOH-d_4 is consistent with the presence of mostly **3a_open** in this solvent. In contrast to **3a**, the ^{31}P{^{1}H} NMR resonance in boron-free **4** shifts downfield with progressively more HB donating solvents[16] (Figure 1b) due to the increasingly deshielded ^{31}P nucleus. ^{11}B NMR spectra of **3a** also show a downfield shift in

stronger HB donor solvents, consistent with the presence of 3-coordinate boron (Figures S4–S6).

Interestingly, in CD$_2$Cl$_2$ the IR spectrum of **3a** shows two P=O stretching peaks at 1196 and 1120 cm^{-1} (Figure S1d). The former is close to $\nu_{P=O}$ of **4** at 1187 cm^{-1}, corresponding to the presence of a free P=O group in **3a_open**, while the latter is due to the presence of **3a_closed**. This is indicative of the coexistence of both structures in this weak HB donating solvent. In CDCl$_3$, only a single broadened ^{31}P peak (δ = 26.2 ppm, peak width = 12.6 Hz) is observed due to rapid equilibration between **3a_open** and **3a_closed** in this solvent. The equilibrium responds to the addition of an external Lewis base such as fluoride anion. Reaction of **3a** in either CDCl$_3$ or acetone-d_6 solution with tetrabutylammonium fluoride (TBAF) results in an upfield shift, and sharpening, of the ^{31}P resonance (from δ = 26.1 to 21.7 ppm in CDCl$_3$ and from δ = 33.4 to 19.6 ppm in acetone-d_6). This is attributed to cleavage of the B–O bond and formation of a fluoride adduct at boron (Figure S2).

Compound **3b** behaves similarly to **3a** in various solvents (Figure S3a). Moreover, the phosphine oxide moiety on **3b** has well-defined ^{1}H NMR signals due to the isopropyl substituents that allow the intramolecular through-space interaction between the Lewis acid and base groups to be probed with NOESY experiments. In methanol-d_4, a NOE was not detected between the CH and CH$_3$ groups on the *i*-Pr moiety and the methyl groups on the Mes$_2$B unit (Figures S7 and S8), consistent with the spatial separation of these groups in **3b_open**. In contrast, in the non-HB solvent benzene-d_6, NOE interactions were observed (Figures S11 and S12), indicating proximity of these groups in agreement with the closed structure **3b_closed**.

The similarities between the behavior of **3a** and **3b** shows that bithiophene-based Lewis pair systems with either aryl or alkyl phosphine oxide substituents show flexible switching between Lewis adducts and unbound Lewis pairs in response to HB donating solvents. By introducing mesityl groups on both Lewis acid and base centers (**3c**) the Lewis adduct can be prevented from forming. Similarly to B-free phosphine oxide **4**, the ^{31}P{^{1}H} NMR resonance of **3c** shifts downfield with more HB donating solvents, with no indication of Lewis adduct formation in any solvent (Figure S3b).

The absorption spectrum of **3a** depends on the HB donor ability of the solvent (Figure 2). In very weak or non-HB donor solvents such as hexanes, the spectra show a dominant band at ~370 nm; however, with increasing HB donor strength (dichloromethane < CHCl$_3$ < MeOH),[14] this absorption band becomes weaker, and the bands between 260 and 350 nm strengthen. In MeOH, the absorption spectrum is similar to that
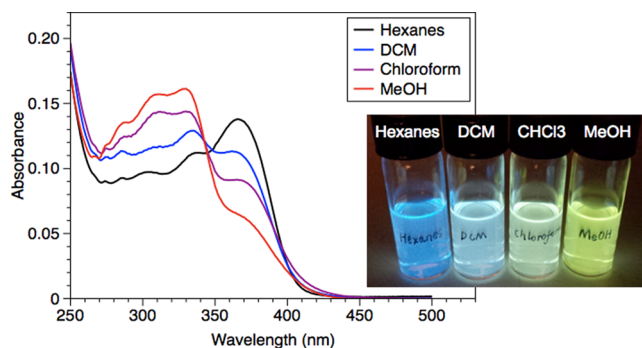

Figure 2. UV–vis spectra of **3a** in various solvents. Inset: Emission from **3a** (λ_{ex} = 366 nm, 18.4 W UV lamp).

observed previously for a boryl-substituted bithiophene,[6d] where the absorption is assigned as a charge-transfer band involving the 3-coordinate Lewis acidic boron center. The same trend is observed in the absorption spectra of **3b**, while those of **3c** show no significant solvent dependence due to the persistent unbound nature of **3c**.

The emission of **3a** is also solvent dependent (Figure 3). In MeOH, **3a** shows strong emission at 540 nm (Figure 3a, red
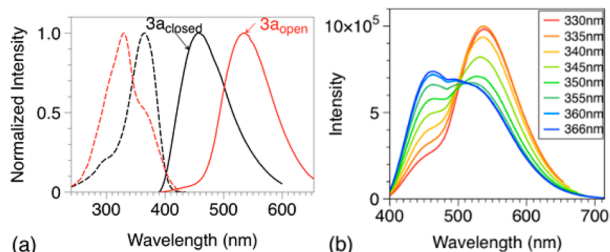

Figure 3. (a) Normalized emission and excitation spectra of **3a**closed in hexanes (black trace) and **3a**open in methanol (red trace). (b) Excitation energy-dependent mixed emission from **3a**open and **3a**closed in CHCl3.

trace) with a quantum yield of 0.60. The relatively large Stokes shift (13400 cm^{-1}) is consistent with a CT excited state in **3a**open as the source of the emission. In hexanes, **3a** shows bright blue emission with a smaller Stokes shift (5050 cm^{-1}) assigned to decay of a bithiophene-localized excited state. In weak HB donating solvents such as CH$_2$Cl$_2$ and CHCl$_3$, compound **3a** luminesces with mixed color. Emission spectra of **3a** in CHCl$_3$ show excitation-dependent luminescence (Figure 3b) with higher energy excitation resulting in lower energy emission. This unusual behavior is the result of simultaneous emission from both **3a**closed and **3a**open; at different excitation wavelengths the two compounds contribute differently to the total output. In contrast, dissolving **3c** in any of the solvents used here results only in intense CT emission coincident with that of **3a**open since the Lewis adduct is not able to form in this case. The emission spectra of **3a** in *n*-butanol, *s*-butanol, and *t*-butanol show an increase in the blue region near 440 nm concomitant with an increase in the steric bulk of the butanol solvent (Figure S14). This is due to a decrease in the strength of the HB donating ability of the solvent[16] resulting in more of the closed structure **3a**closed being present.

The emission of **3a** is highly temperature-dependent in alcohol solvent. At room temperature, where **3a**open is the major species present in strong HB donor solvents, the dominant emission from **3a** is at ~540 nm. However, with cooling, the emission band at 440 nm (assigned to **3a**closed) increases in intensity with a concomitant decrease in the band at 540 nm (Figure 4a). The variable temperature ^{31}P{^{1}H} NMR spectra of **3a** in methanol-*d*$_4$ show significant downfield shifts and broadening as more **3a**closed forms at lower temperatures, while the ^{31}P{^{1}H} NMR spectrum of boron-free compound **4** shows only slight broadening and upfield shifts over the same temperature range (Figure 4b). The observed temperature dependence of the **3a**closed/**3a**open equilibrium is possibly due to the decrease in entropy resulting from the increased rigidity of **3a**closed relative to **3a**open.

DFT computational studies (using all-electron TZ2P basis sets at the BP86 level) confirmed that **3a**open and **3a**closed both correspond to minima on the ground state potential energy surface (Figure S16). The calculated B−O distance increases from 1.64 Å in **3a**closed to 3.67 Å in **3a**open, and the S−C−C−S dihedral angle also significantly increases from 23.4° in **3a**closed to

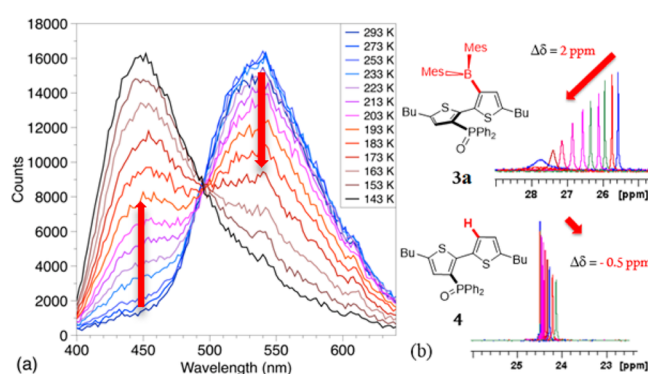**Figure 4.** (a) Variable temperature emission spectra of **3a** in a MeOH/EtOH (v/v = 1:4) solution, excited at 330 nm. (b) Variable temperature ^{31}P{^{1}H} NMR spectra of **3a** and **4** in CD$_3$OD (−65 to 25 °C at 10 °C intervals).

65.0° in **3a**open. Single-point calculations of the ground-state structures confirmed that the LUMO of **3a**closed is mostly bithiophene-localized, while the LUMO of **3a**open is strongly boron-centered (Figure 5).
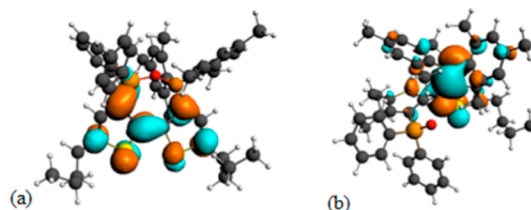

Figure 5. LUMO diagrams of (a) **3a**closed and (b) **3a**open.

TD-DFT calculations (using PBE0 hybrid functional and all-electron TZ2P basis sets) were used to calculate absorption transitions for both **3a**closed and **3a**open. These show that the lowest energy absorption of **3a**closed involves a bithiophene-localized π−π* transition mixed with a charge transfer transition from a mesityl π-orbital to the LUMO. The lowest energy absorption in **3a**open arises from charge transfer processes from a mesityl-localized π-orbital and a bithiophene-localized π-orbital to the boron-centered LUMO. This indicates that **3a**open and **3a**closed are expected to exhibit different absorption spectra, consistent with the UV−vis spectra in Figure 2.

In conclusion, we report here flexible Lewis pairs **3a** and **3b** that undergo a temperature- or solvent-dependent structural change. ^{31}P and ^{11}B NMR shifts and P═O stretching frequencies are used to track the structural changes. We demonstrate an unusual reversible system where various interactions between Lewis acidic and basic moieties on a π-conjugated system give rise to different light absorbing and luminescence properties. The formation of the open structure is driven by hydrogen bond formation with the solvent, which stabilizes the free P═O bond. Investigations of the potential application of these systems in switchable Lewis acid catalysis, photocatalysis, and sensing are underway.

■ **ASSOCIATED CONTENT**

S **Supporting Information**

Spectroscopic data for new compounds, experimental and computational details, and additional data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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