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View Article Online DOI: 10.1039/C4CC08958H

Structural diversity of new solid-state luminophores based on quinoxaline- β -ketoiminate boron difluoride complexes with remarkable fluorescence switching properties

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s Received (in XXX, XXX) Xth XXXXXXX 20XX, Accepted Xth XXXXXXXX 20XX DOI: 10.1039/b000000x

A series of structurally simple yet highly tunable organoboron luminophores was designed and synthesized. The solid-state fluorescence quantum yields exhibit nearly exponential or growth by decorating the luminophore with additional steric demanding substituents. Uniquely, the luminescence of these organoboron dyes can be easily switched on/off by acidic/basic vapors, yielding a solid-state fluorescence switching function.

- ¹⁵ Organic solid-state luminescent materials have received increasing attentions in recent years because of their potential applications in optoelectronics,^{1, 2} optically pumped lasers,³ and fluorescent sensors.⁴ Of special note, external stimuli-responsive tuning of solid-state fluorescence based on the phase ²⁰ transformation of single substrate, which render them the possibility of versatile applications in the field of optical recording material and security inks.⁵ Known to possess intriguing optical properties such as high absorption coefficients and fluorescence quantum yields, organoboron complexes are one
- ²⁵ of the most crucial fluorescent dyes which show tunable absorption/emission profiles as well as excellent chemical and photochemical stability.⁶ In the perspective of these attractive features, considerable efforts have been devoted to the development of various fluorescent organoboron complexes with
- ³⁰ a variety of applications spanning from bio-labeling' to photovoltaics,⁸ laser dyes,⁹ and molecular probes.¹⁰

However, the common boron dipyrromethene (BODIPY) derivatives normally suffer from drawbacks such as feeble solidstate emission attributed to the notorious π - π interactions leading

- ³⁵ to formation of excimers and exciplexes¹¹ and small Stokes shifts (400-600 cm⁻¹ in most cases) which results in self-absorption of its own fluorescence. Moreover, the interference by excitation and scattering light renders the fluorescence signal difficult to separate from the background noise in a bioassay.¹² While a few
- ⁴⁰ boron complexes were reported towards addressing these issues,¹³ it is still highly desirable to develop next-generation organoboron

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† Electronic Supplementary Information (ESI) available: experimental details, characterization data, UV-vis, fluorescence spectra, details of crystal analysis and photographs. See DOI:10.1039/b000000x/ 50 complexes with high solid-state emissions along with large Stokes shifts aiming to gain meaningful insights and establish indepth structure-property relationship, which would pave the ways for practical applications. In combination of the unique aggregation-induced emission enhancement (AIEE) 55 phenomenon¹⁴ and the intriguing properties associated with unsymmetry boron complexes possessing enhanced solid-state emission and large Stokes shifts,¹⁵ we report here a series of quinoxaline- β -ketoiminate derivatives and their corresponding boron complexes (Scheme 1) which show remarkable 60 luminescent properties in both solid state as well as in solution. As envisaged, phenyl substituted derivatives exhibited strong solid-state luminescence due to the structural twist exerted by the additional phenyl substitution.5n Moreover, the luminescence of these organoboron compounds can be easily switched on/off by 65 acidic/basic vapors, yielding a solid-state acid/base fluorescence indicator.16



Scheme 1. Synthetic routes of quinoxaline- β -ketoimnate ligands **1a-5a** and their ro corresponding boron difluoride complexes **1-5**. Inset depicts the overlapped crystal structures of **1** (pink), **2** (orange), and **4** (green).

All new quinoxaline- β -ketoimnate ligands and their 75 corresponding boron complexes were fully characterized by various spectroscopic techniques. Details of the experimental procedures and data for structural characterization are described in the Supplementary Information. The key precursors,

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quinoxaline- β -ketoiminate derivatives **1a-5a**, were obtained by the reaction of quinoxaline derivatives **6-8** with the corresponding aryl ester in the presence of sodium hydride. Noticeably, these ligands showed a distinctively downfield (~13 ppm) shifted ¹H

- s NMR signal for the H-bonded enol proton. Unlike previously reported pyrazine-based β-ketoiminates,^{13b} ligands **1a-5a** did not exhibit keto-enol tautomerism in the ¹H NMR except for triphenylamine substituted derivatives. Treatment of the resulting quinoxaline- β -ketoiminate ligands **1a-5a** with boron trifluoride
- ¹⁰ diethyl etherate in the presence of triethylamine in dichloromethane gave the desired boron complexes **1-5** in high yields (see SI). In the ¹H NMR spectroscopy, the disappearance of the intramolecular H-bonded enol proton signal at ~13 ppm readily supports the BF₂ complexation which is further confirmed ¹⁵ through mass spectra. The ¹¹B spectra appear well-defined triplets due to the coupling with the two ¹⁹F nuclei and the chemical shifts are in the range of 2 to 2.5 ppm. The resonances for the fluorine atoms appear as a 1:1:1:1 quartet at ~ -126 ppm in the ¹⁹F NMR spectra due to the coupling with boron (see SI).
- The redox property of complexes 1-5 was investigated by cyclic voltammetry (CV) in dichloromethane (Table S1). All boron complexes exhibited a single reversible reduction between -1.07 and -1.20 V (vs. Fc/Fc⁺), which is comparable to the reduction of the structurally similar BODIPY core.¹⁷ The 25 reduction is consistently and moderately correlated to the aryl (R') substituents depending their electron on donating/withdrawing ability. One irreversible oxidation at ~1.5 V (vs. Fc/Fc^{+}) for all boron complexes was observed except for complexes 3 and 5 which showed an additional reversible $_{30}$ oxidation at ~0.6 V (vs. Fc/Fc⁺) ascribed to the oxidation of TPA (Fig. S1). The suitable LUMO and HOMO energies for all compounds estimated by CV may find potential applications in organic photovoltaics.⁹

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- All new boron complexes were structurally characterized by ³⁵ X-ray crystallography. The overlapped crystal structures of **1**, **2** and **4** are depicted in Scheme 1. The bond distances of B1-O1 are around 0.13 Å longer than those of B1-N1 in crystal structures presumably in reflection of the electronegativity of the oxygen atom and the unsymmetrical nature at the boron center. The ⁴⁰ crystal structures of **1**, **2** and **3** reveal a nearly planar
- 40 Crystal structures of 1, 2 and 5 reveal a hearly planar conformation between the quinoxaline unit and the phenyl/triphenylamino substituent (R'). Compared to the unsubstituted and methyl substituted analogues, the presence of additional phenyl substituents results in obvious non-planarity in 45 the molecular structures of 4 and 5 with dihedral angles of
- ~57.89°, ~44.14°, respectively (Table S3). We are able to further deduce the structure-property correlations of H-, methyl- and phenyl-substituted boron complexes in solution and solid state by the analysis of their photophysical properties and crystal packing ⁵⁰ patterns.
- The photophysical properties of boron complexes 1-5 were studied in solvents of varying polarity. The absorption spectra of 1, 2, and 4 were hardly affected by solvent polarity (Table S2). The emission maximum displayed slightly bathochromic shift ⁵⁵ when solvent was changed from nonpolar hexane to polar CH₃CN. The insensitivity of the absorption and emission spectra toward solvent polarity suggests negligible change of the dipole moments between their ground and both Franck-Condon and relaxed excited states. However, the absorption spectra were red-⁶⁰ shifted about ~10 nm switching from methyl (2) to phenyl substitution (4). The absorption spectra of 1, 2, and 4 recorded in CHCl₃ showed distinct fine structures between 400-450 nm (Fig. 1a), which are characteristic of typical π - π * transitions with notable vibronic features and high extinction coefficients (~10⁴ M^{-1} cm⁻¹). In a sharp contrast, 3 and 5 exhibited a broad and red-

shifted band in the range of 500-550 nm attributed to an intramolecular charge transfer (ICT) transition between the triphenylamine donor group and the acceptor BF₂ monety if Fightine 1a). Akin to the absorption spectra, the emission maxima of **3** and **5** were also shifted toward longer wavelength than those of **1**, **2**,

and 4 (Fig. 1b) due to the presence of low-lying ICT transition, which also resulted in lower fluorescence quantum yields for complexes 3 and 5 than others. In sharp contrast to the minor solvent dependent spectral features of 1, 2, and 4, the emission 75 spectra of the donor-acceptor molecules, 3 and 5, exhibited prominent solvatochromic effect with a monotonic bathochromic shift upon increasing the solvent polarity indicative of large dipole moment in the excited state (Table S2).



Fig. 1 Absorption (a) and emission (b) spectra of 1-5 recorded in $CHCl_3$ (5 \times 10^{-6} M).

 85 Table 1 Photophysical data of complexes 1-5 recorded in CHCl3 solution (5 \times 10 $^{-6}$ M) and solid state

Dyes	λ_{abs} , nm (log ϵ)	λ _{em} (nm)	Δ (cm ⁻¹)	τ (ns)	${\displaystyle \oint} {\displaystyle (\%)}^{ m a}$	${\scriptstyle \Phi} {\scriptstyle (\%)}^{ m b}$	$\left(nm \right)^{b}$
1	410 (4.2), 434 (4.4), 459 (4.4)	475	733	4.13	92	2.0	580
2	405 (4.3) 427 (4.5), 452 (4.4)	467	711	2.75	81	9.1	537
3	510 (4.6)	605	3079	2.92	30	1.8	624
4	417 (4.3), 439 (4.5), 466 (4.4)	482	713	2.50	78	22	523
5	525 (4.6)	617	2840	2.44	10	9.3	620

^{*a*}Quantum yields in solution were determined by using 9,10-diphenylanthracene (1, 2, 4) or Rhodamine 6G (3, 5) as the references. ^{*b*}Measured by the integrated sphere method in solid state.

All boron complexes 1-5 showed red-shifted emission in solid state with respect to the corresponding emissions in solution, which is attributed to the increasing intermolecular interactions (Table 1). The bulkiness of the substituent (**R**) on the quinoxaline 95 exhibits an apparent correlation to the solid-state quantum yield whereas no positive correlation exists for such substituent effect with R' groups. The complexes with phenyl substituent (R) showed higher solid-state emission quantum yields in comparison to their unsubstituted and methyl substituted analogues. In CHCl₃ ¹⁰⁰ solution, fluorescence quantum yields follow the order of 1 (92%) > 2 (81%) > 4 (78%) whereas a reverse order of fluorescence quantum yields was observed in solid state with 4 (22%) > 2(9.1%) > 1 (2.0%). Moreover, the emission maxima in solid state also follows a trend in which 1 (580 nm) > 2 (537 nm) > 4 (523 105 nm) (Table 1). In order to pinpoint the structure-property relationship of distinct photophysical properties of 1, 2 and 4, a comparison of the molecular arrangements in the crystal structures was investigated. Various secondary bonding interactions (π - π , C-H···F, C-H··· π , and C-H···N interactions) play 110 critical roles in molecular stacking assemblies in crystal structures 1-5. Crystal 1 is organized in two independent crystal stacks and the molecules are arranged as dimers in a head-to-tail

^{2 |} Journal Name, [year], [vol], 00-00

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manner. The $\pi - \pi$ distance is 3.588 Å in the dimer of *Column B* whereas the counterpart is 3.885 Å in *Column A* (Fig. S7). Apart from the strong $\pi - \pi$ interactions, the interplays of eight C-H…F hydrogen bonds in the range of 3.263-3.545 Å (\angle C-H…F =

- s 138.66°-166.00°) and additional C-H…N and B-F…π (quinoxaline) dipole-dipole interactions govern the overall crystal packing in complex 1 (Table S3). Methyl analogue 2 exhibits an intermolecular π−π distance of 3.620 Å and three C-H…F interactions in the range of 3.153-3.473 Å (∠C-H…F = 119.56°-
- ¹⁰ 164.88°). Furthermore, an additional C-H···N interaction also contributes to the overall crystal packing in 2. Interestingly, phenyl substituted derivative 4 displays the longest π-π distances of 3.649 and 3.717 Å and one of the intermolecular H-bond (C18-H18···F1, 3.244 Å, 129.1°) constrain the rotation which may
 ¹⁵ further uplift π-π distance due to its vertical direction. The subtle difference in the crystal packing patterns by changing the substitution from -H to -Me to -Ph effectively minimizes the intermolecular interactions. The decrease in the extent of π-π overlap in the structural packing of complex 4 compared to ²⁰ complexes 1 and 2 (Fig. S10) leads to a hypsochromic emission in solid state along with high fluorescence quantum yields instead of producing detrimental excimer-like emission (Fig. 2). The π-π interactions and dihedral angles summarized in Table 2 unambiguously support our conclusion.



Fig. 2 Packing diagrams of crystals (a) 1, (b) 2, (c) 4. (d) Solid-state emission spectra of 1-5.

Table 2. The π - π interactions and dihedral angles in single crystals 1-5

Dyes	π–π (Å)	Dihedral angles (°) ^{a, b}	
1	3.589, 3.885	A-4.18 ^a , B-3.57 ^a	
2	3.620	5.37ª	
3	3.625, 3.656, 3.660, 3.698	12.06 ^a	
4	3.649, 3.717	12.72 ^a , 57.89 ^b	
5	3.646, 3.725	22.05 ^a , 44.14 ^b	
			-

[a] The dihedral angle between the quinoxaline-BF₂ core and phenyl/triphenylamino substituent (\mathbf{R}^{\prime}). [b] The dihedral angle between the quinoxaline-BF₂ core and additional phenyl substituent (\mathbf{R}).

A similar trend was observed for the -Me (3) and -Ph (5). Compared to complex 3, complex 5 has a longer π - π intermolecular distance in the dimer and the degree of overlap between adjacent dimers are quite different in spite of π - π ⁴⁰ interactions are also formed in adjacent dimers (Fig. S9). The twisted conformation of crystal 5 significantly impedes the intermolecular interactions and results in minor red shift in solidstate fluorescence with high quantum yield (Table S3). Nevertheless, the head-to-tail arrangement of the molecular ⁴⁵ packing mode in complex 5 undesirably introduces intermolecular charge transfer interaction, which likely become an extra excited-state energy deactivation channel to result in a lower solid-state emission quantum yield than complex 4 despite the intermolecular π - π distances in complexes 4 and 5 are comparable. Notably, the AIEE-active ICT emitter in complex 5 was supported by the UV and emission spectra in THF-water mixture (Fig. S11). The Mie scattering effect observed in the visible absorption spectra of 5 implied that the nanoparticles of the aggregated process were formed in the mixtures with water sf fraction up to 80%. The slightly blue-shifted emission (80% water fraction) could be attributed to the formation of nanoaggregates with twisted conformation and suppressed the ICT character.

Most interestingly, the boron complexes 1-5 possess unusual 60 acidochromic behavior triggered by acid vapor, which holds the potential to develop into a solid-state fluorescence switching material. After exposure to trifluoroacetic acid (TFA) vapors, the colors of 1-5 turned into obscure and absorption spectra were redshifted accompanied by strong quenching of luminescence. The 65 fluorescence can be switched between "on" and "off" by treating with triethylamine (TEA)/TFA vapors in spite of slight attenuation of luminescence (Fig. 3 and Fig. S12-S13). The fluorescence quenching upon acid fuming is attributed to the synergistic effects: (i) the protonation of nitrogen of pyrazine 70 segment induces push-pull effect and further enhances the ICT transition and (ii) the changes of intermolecular packing and molecular conformation upon acid protonation may transform the ⁷⁵ diffraction patterns (Fig. S14).¹⁶ recursive unrough enhanced crystalline powder into an amorphous state through enhanced



Fig. 5 (a) images of 4 taken under haked eye and 0.V tahip ($v_{ex} - 50$ hm). The samples were deposited on a slide glass. (b) Fluorescence spectra of 4 between "on" so and "off" by reversibly treated with TEA/TFA vapors in solid state. (c) Recycling of the fluorescence switching of solid powder 4 upon fuming with TFA and TEA vapors (I₀ is the original PL intensity and I is the PL intensity of 4 after fuming with TFA or TEA).

In summary, we have developed new quinoxaline- β ketoiminate boron difluoride complexes possessing tunable and fascinating photophysical properties by simple decorating the luminophore with various substitutions. These complexes displayed high fluorescence quantum yields in solution. In 90 particular, the solid-state fluorescence of these complexes is enhanced by an order of magnitude upon changing the substituent from -H to -Me to -Ph. Moreover, a large Stokes shift has been achieved for triphenylamine substituted analogues. Such results demonstrate that these complexes are of paramount significant for 95 the design of efficient solid-state emitter and suitable for promising applications in solar cells and organic light-emitting transistors.¹⁸ Most uniquely, complexes 1-5 exhibit a reversible on-off solid-state luminescence switching by acid/base fuming processes, which might pave the way for future fluorescent 100 molecular switches.

Acknowledgements

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We are grateful to the Ministry of Science and Technology of Taiwan (Grant No MOST 103-2113-M-001-026-MY3) and Academia Sinica for support of this research. Dr. Yu-Sheng Wen at Institute of chemistry, Academia Sinica and Mr. Ting-Shen ⁵ Kuo at National Taiwan Normal University are acknowledged for their help in crystal structure refinements.

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