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Turning on Fluorescent Emission from C-Alkylation on Quinoxaline Derivatives

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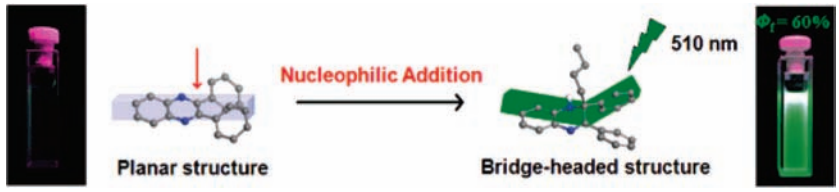
ABSTRACT



Reduction on imine moiety (C═N) of quinoxalines by alkyl-/aryllithiums led to a geometrical change on the quinoxaline ring, thereby perturbing the electronic structure to turn on fluorescence emission. Such a structural change resulted in interrupted cyclic-ring systems with electron-donating amine (sp^3-type) and electron-accepting imine (sp^2-type) units bridged by a phenylene unit. Through either alkylation or arylation, a highly polarized electron donor−electron acceptor bipolar system was established in a single molecule with dramatically enhanced PL efficiency (up to 60%).

Since the discovery of organic light emitting diodes (OLEDs) by Tang[1] and Burroughes,[2] there has been substantial effort aimed at developing highly efficient electroluminescent (EL) materials. In particular, small molecules with a built-in donor−acceptor architecture have currently attracted considerable attention as the key emissive elements due to their good properties such as bipolar charge (electron and hole) transport and high PL efficiency.[3,4] As representative examples, many groups have reported several electron donor−acceptor (ED-EA) conjugated compounds as emissive OLED materials, which are combined with triarylamine,[4] carbazole,[5] fluorene,[4c] and phenoxazine/-thiazine[6] as a donor and oxadiazole,[4,7] benzothiadiazole,[8] diarylboron,[3] and phenylquinoline[9] as an acceptor. Recently an electro-deficient quinoxaline moiety has been actively used as the acceptor to obtain high-efficiency bipolar luminescent materials due to its great diversity of tunable electronic properties resulting from ligand substitution, where the systematic alteration is mainly carried out by incorporating electron-donating groups to the 2,3-[5b,10] or 5,8-position[11] of the quinoxaline moiety.

(1) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.
(2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Homes, A. B. *Nature* **1990**, *347*, 539.
(3) (a) Shirota, Y.; Kinoshita, M.; Noda, T.; Okumoto, K.; Ohara, T. *J. Am. Chem. Soc.* **2000**, *122*, 11021. (b) Doi, H.; Kinoshita, M.; Okumoto, K.; Shirota, Y. *Chem. Mater.* **2003**, *15*, 1080.
(4) (a) Hamada, Y.; Adachi, C.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1992**, *31*, 1812. (b) Tamoto, N.; Adachi, C.; Nagai, K. *Chem. Mater.* **1997**, *9*, 1077. (c) Antoniadis, H.; Inbasekaran, M.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 3055.
(5) (a) Zhu, W.; Hu, M.; Yao, R.; Tian, H. *J. Photochem. Photobiol., A* **2003**, *154*, 169. (b) Thomas, K. R. J.; Lin, J. T.; Tao, Y.-T.; Chuen, C. H. *J. Mater. Chem.* **2002**, *12*, 3516.
(6) (a) Lai, R. Y.; Fabrizio, E. F.; Lu, L.; Jenekhe, S. A.; Bard, A. J. *J. Am. Chem. Soc.* **2001**, *123*, 9112. (b) Zhu, Y.; Kulkarni, A. P.; Jenekhe, S. A. *Chem. Mater.* **2005**, *17*, 5225.
(7) Thomas, K. R. J.; Lin, J. T.; Tao, Y.-T.; Chuen, C.-H. *Chem. Mater.* **2002**, *14*, 3852.
(8) Thomas, K. R. J.; Lin, J. T.; Velusamy, M.; Tao, Y.-T.; Chuen, C.-H. *Adv. Funct. Mater.* **2005**, *15*, 231.
(9) (a) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 895. (b) Zhang, X.; Shetty, A. S.; Jenekhe, S. A. *Macromolecules* **1999**, *32*, 7422. (c) Jenekhe, S. A.; Zhang, X.; Chen, X. L. *Chem. Mater.* **1997**, *9*, 409.
(10) (a) Chen, C.-T.; Lin, J.-S.; Moturn, M. V. R. K.; Lin, Y.-W.; Yi, W.; Tao, Y.-T.; Chien, C.-H. *Chem. Commun.* **2005**, 3980. (b) Thomas, K. R. J.; Velusamy, M.; Lin, J. T.; Chuen, C.-H.; Tao, Y.-T. *Chem. Mater.* **2005**, *17*, 1860. (c) Kulkarni, A. P.; Zhu, Y.; Babel, A.; Wu, P.-T.; Jenekhe, S. A. *Chem. Mater.* **2008**, *20*, 4212.

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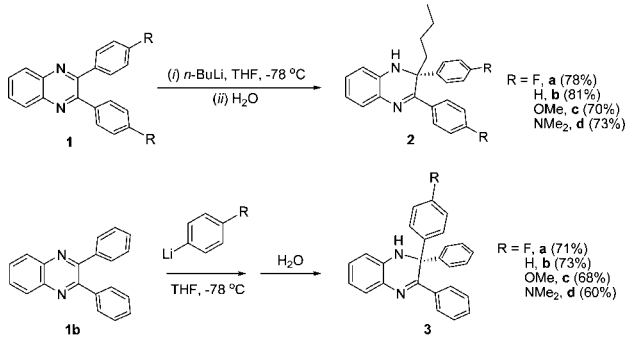
This study examined new types of quinoxaline-based bipolar systems as a part of an ongoing study into the development of highly emissive materials based on the concepts of ED-EA. In general, it has been noted that reactions of organolithium such as *n*-butyllithium with pyridine led ultimately to 2-butylated products, and the subsequent hydrolysis produced 2-butyl-1,2-dihydropyridine with efficient change of the sp^2-type nitrogen center (EA) into a sp^3-type nitrogen (ED).[12] Given the fact that nucleophilic addition adjacent to the electro-negative element (e.g., nitrogen) in the conjugated ring is possible, such a reaction can also be applied to the quinoxaline system. Indeed, when the addition reaction was carried out by reacting quinoxaline with an alkyl/aryllithium reagent, the expected alkyl/aryl-added products were produced in high yields (60−81%). With this reaction scheme in hand, a series of 2-alkyl/arylated quinoxaline compounds 2-butyl-2,3-diarylX-1*H*-quinoxaline (**2**) and 2-arylX-2,3-diphenyl-1*H*-quinoxaline (**3**) were produced, where the 2,3-postion of the products was altered by the *para*-substituted aryl-X groups (X = F, H, OMe, and NMe_2). Through this substitution, efficient ED-EA-type materials were produced, turning on fluorescent emission with the red-shifed PL emission (~510 nm).

2,3-Disubstituted quinoxalines (**1**) were prepared by Suzuki−Miyaura coupling reaction[13] or condensation of *o*-phenylenediamine and 1,2-substituted dicarbonyl compounds.[14]From the reaction of **1** with *n*-butyllithium and

Scheme 1. Synthesis of 2-Alkyl/Arylated Quinoxaline Compounds **2** and **3**



subsequent hydrolysis, a series of electronically tuned 2-butyl-2,3-diaryl-1*H*-quinoxaline (**2**) was synthesized in good yields (Scheme 1). As shown in Scheme 1, the desired 2-ArX-2,3-diphenyl-1*H*-quinoxaline (**3**) were prepared from a reaction of **1b** (1 equiv) and LiArX (1.1 equiv) *para*-substituted with X = NMe_2, OMe, H, and F. In all cases, the products were isolated by flash chromatography in good yields (60−81%). Single crystals were obtained by recrystallization of the compounds from the solution of CH_2Cl_2/hexane (v/v = 1/2).

X-ray analysis of **3d** was carried out to establish the structure of the 2-alkyl/arylated quinoxaline compounds. As shown in Figure 1, the geometrical change derived from the

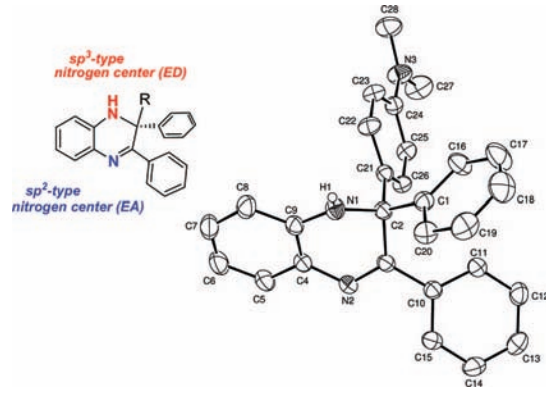


Figure 1. X-ray crystal structure of **3d**.

substitution of the 4-dimethylaminophenyl unit efficiently produced a pseudotetrahedral geometry different from that found in general quinoxaline derivatives, confirming the addition of the 2-aryl group on quinoxaline derivatives. As shown in Table S2 in Supporting Information, four bond angles around the 2-carbon center authenticated a typical tetrahedral geometry having values in the ranges of 110.4(1)−113.0(1)°. Saturation of the N(1)−C(2) double bond (1.475(2) Å) by aryl and hydrogen groups induced a structural transformation from planar to bridge-headed geometry with an interrupted cyclic-ring system, where the electron-donating amine (sp^3-type) and electron-accepting imine (sp^2-type) units are conjugated by phenylene unit. A subsequent electron density difference might result in a significant change in the electronic structure of quinoxaline derivatives.

The UV−visible absorption and fluorescence spectra of **1** and **2** were measured in chloroform, and the data is summarized in Table 1. A substantial structural change in the core luminescence unit was expected on the basis of the characteristic changes in absorption and emission spectra.

Upon C-alkyl/arylation of the quinoxaline C=N functional group, the symmetrical quinoxaline fused ring system transformed into a puckered interrupted ring to create the unsymmetrical structures observed in **2** and **3**. This perturbed ring is believed to be the origin of the photoluminescence turn-on.

The formation of an unsymmetrical structure by C-alkyl/arylation gave rise to the typical intramolecular charge transfer (ICT) emission with a dramatically enhanced PL efficiency (up to 60%). As shown in Table 1, in general,

(11) (a) Aldakov, D.; Palacios, M. A.; Anzenbacher, P., Jr. *Chem. Mater.* **2005**, *17*, 5238. (b) Mancilha, F. S.; Neto, B. A. D.; Lopes, A. S.; Moreira, P. F., Jr.; Quina, F. H.; Gonçalves, R. S.; Dupont, J. *Eur. J. Org. Chem.* **2006**, *n/a*, 4924. (c) Chen, C.-T.; Wei, Y.; Lin, J.-S.; Motoru, M. V. R. K.; Chao, W.-S.; Tao, Y.-T.; Chien, C.-H. *J. Am. Chem. Soc.* **2006**, *128*, 10992.

(12) (a) Armstrong, D. R.; Mulvey, R. E.; Barr, D.; Snaith, R.; Reed, D. *J. Organomet. Chem.* **1988**, *350*, 191. (b) Moudam, O.; Ajamaa, F.; Ekouaga, A.; Mamlouk, H.; Hahn, U.; Holler, M.; Welter, R.; Nierengarten, J.-F. *Eur. J. Org. Chem.* **2007**, *n/a*, 417.

(13) Mao, L.; Sakurai, H.; Hirao, T. *Synthesis* **2004**, *n/a*, 2535.

(14) Eicher, T.; Hauptmann, S. *The Chemistry of Heterocycles*; Thieme: New York, 1995; pp417−422 and 434.

2-alkylated quinoxaline compounds **2** show considerable bathochromic shifts in both UV and PL spectra centered at around 380 and 510 nm, respectively, when compared to those of parent quinoxalines **1**. However, in the case of **1d**, such a shift is not pronounced as a result of the prescence of strong bipolar character in a single molecule. There exists an ICT character between the electron-deficient pyrazine ring and the electron-donating 2,3-(4-dimethylamino)phenyl moiety. A similar bathochromic trend was also observed in the

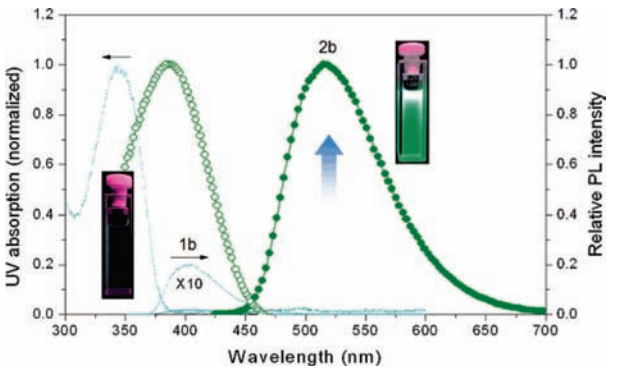


Figure 2. Increased Stokes shift and fluorescence turn-on via C-butylation of quinoxaline C═N found in **2b**.

series of 2-arylated compounds **3a**−**d**, exhibiting UV absorption and PL emission maxima in the range of 373−377 and 514−525 nm, respectively. Furthermore, the larger Stokes shift highlights the ICT character of the fluorescent states of the 2-alkyl/arylated quinoxaline compounds.[15] Depending on the variation of solvent polarity, the 2-alkylated quinoxaline compounds showed large positive solvatochromic shift indicating strong intramolecular donor−acceptor interactions (Figure 3 and Table S3 in Supporting Information).[16] This result can be explained by the formation of ED-EA in a single molecule with sp^3- and sp^2-amine/imine functionalities. In addition, arylated compounds **3** showed similar UV and PL spectra regardless of the *para*-substituents on the ArX group, where X varied from F to NMe_2. This might be due to inefficient charge delocalization rising from the placement of nonplanar sp^3 carbon in an ED-EA single molecule.[17]

CVs of 2,3-substituted quinoxaline compounds (**1**) with electron-donating/-withdrawing groups show no reversible peaks arising from the oxidation potential but a redox peak arising from reduction at around −2.10 V. This was attributed to the electron-deficient pyrazine ring containing two sp^2-type centers (Figure 4 and Figure S4 in Supporting Information). For the 2-alkyl/arylated quinoxaline compounds **2** and **3**, the oxidation potentials is shifted to a positive range (∼0.3 V) with increasing electron donor strength, as the electron-accepting imine (sp^2-type) unit was changed to an electron-donating amine (sp^3-type). On the other hand, reduction potentials are observed in the higher negative potential range

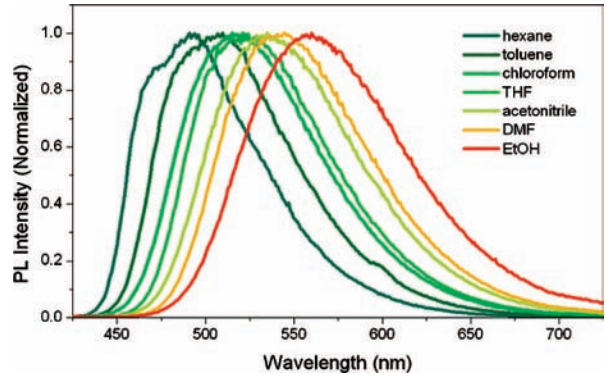


Figure 3. Solvent-dependent emission resulting from the ICT character of the efficient single molecular ED-EA system (**2b**).

Table 1. Photophysical Properties of **1**, **2**, and **3**

sample	UV[a] (λ_{max}/nm)	PL (λ_{max}/nm) solution[a]	PL (λ_{max}/nm) film[b]	Stokes shift (cm^{-1})	Φ_f (%)[a]
1a	346	402	404	4027	*c*
1b	344	398	398	3945	*c*
1c	368	430	432	3919	18
1d	413	518	520	4909	44
2a	385	513	521	6482	58
2b	386	518	522	6603	60
2c	372	511	519	7313	52
2d	399	518	522	5758	38
3a	374	515	507	7321	44
3b	374	514	508	7284	48
3c	373	518	509	7506	47
3d	377	525	518	7478	47

[a] In chloroform. [b] Emission maximum for thin solid film. [c] It was difficult to measure this value due to the low intensity. All photoluminescent spectra were measured at each UV (λ_{max}/nm).

(−2.5 V) due to the sp^2-type nitrogen center. The HOMO and LUMO energy levels were calculated based on the relationship of HOMO/LUMO (eV) = $-e(E_{onset}^{ox}/E_{onset}^{red}$ V (vs Fc/Fc^+) + 4.8 V).[18] The HOMO levels of **1** and **2** increased systematically, as the substituents were changed from electron-withdrawing to electron-donating substituents, up to 0.76 eV difference. However, the LUMO levels were relatively less sensitive with deviation of only ∼0.1 eV

(15) (a) Shizuka, H.; Obuchi, H.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1981**, *n/a*, 405. (b) Shizuka, H.; Sato, Y.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1982**, *n/a*, 439. (c) Shizuka, H.; Sato, Y.; Ueki, Y.; Ishikawa, M.; Kumada, M. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 341. (d) Mac, M.; Danel, A.; Wisła, A.; Karocki, A.; Królicki, R. *J. Photochem. Photobiol., A* **2006**, *180*, 88.

(16) (a) Kollmannsberger, M.; Rurack, K.; Resch-Genger, U.; Daub, J. *J. Phys. Chem. A* **1998**, *102*, 10211. (b) Grabowski, Z. R.; Rotkiewicz, K.; Rettig, W. *Chem. Rev.* **2003**, *103*, 3899. (c) Jenekhe, S. A.; Lu, L.; Alam, M. M. *Macromolecules* **2001**, *34*, 7315. (d) Bhattacharyya, K.; Chowdhury, M. *Chem. Rev.* **1993**, *93*, 507.

(17) Liu, X.-M.; He, C.; Huang, J.; Xu, J. *Chem. Mater.* **2005**, *17*, 434.

(18) Bard, A. J.; Faulkner, L. R. In *Electrochemical Methods: Fundamentals and Applications*, 2nd ed.; John Wiley & Sons, Inc.: New York, 2001, p 54.

(Table S4 in Supporting Information). As a result of the electronic change caused by 2-alkyl/arylation, the HOMO and LUMO levels of **2** were higher and the band gap was lower than those of **1**. A similar trend was observed in the HOMO and LUMO levels of the 2-arylated quinoxaline derivatives **3** and **1b** (Figure S5 in Supporting Information). In addition, the invariant values for **3** are in agreement with those estimated from the edges of the electronic absorption bands. The reduced HOMO−LUMO energy gaps of **2** and **3** showed a good correlation with the red-shifted UV spectra.

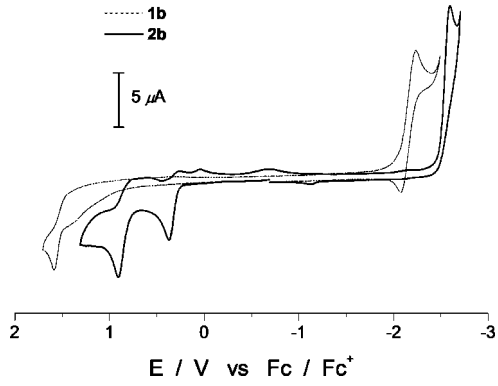


Figure 4. Cyclic voltammograms of 1 mM **2b** (solid line) and **1b** (dashed line) at a platinum electrode ($\Phi = 1$ mm) in CH_3CN solution containing 0.1 M $TBAPF_6$ with $\upsilon = 0.1$ V s^{-1}.

To understand the key factors responsible for the large differences observed in the photophysical and electrochemical properties, quantum chemical calculations for the 2-alkylated quinoxaline derivatives **2** were carried out using DFT as implemented in the *Dmol*^{3} package.[19] Figure 5 summarizes the calculation results and the representative HOMO and LUMO diagram of **1b** and **2b**. The frontier orbitals did not show a significant contribution from the 2-phenyl moiety, which indicates that the tetrahedral geometry around 2-carbon center efficiently blocks the electronic coupling between 2-aryl substituents and nonplanar quinoxaline ring. As shown in Figure 5, HOMO and LUMO orbitals for **1b** are symmetrically spread over the pyrazine ring. In contrast, for **2b** there exist uneven HOMO and LUMO orbital distributions: Pyrazine ring contributes mainly to HOMO orbitals whereas 3-phenyl ring contributes greatly to LUMO orbitals. Localization of the HOMO/LUMO orbitals generally indicates the existence of significant charge-transfer character in the molecule as observed in other ED-EA system.[20] However, in the case of **2b**, it is not clear to identify HOMO and LUMO orbital contributions for sp^3- and sp^2-type nitrogen atoms, respectively.

In summary, nucleophilic addition reaction was successfully engaged in quinoxaline systems to give new types of

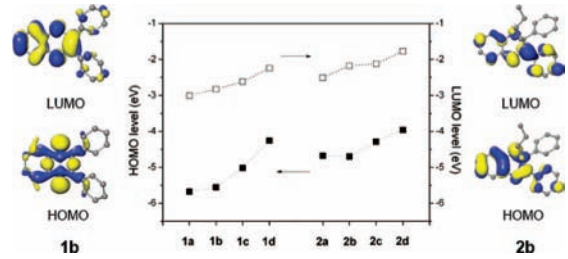


Figure 5. Representative orbital diagram obtained from the *Dmol*^{3} calculation and HOMO−LUMO energy levels of **1** and **2**.

bipolar single molecular donor−acceptor compounds, 2-alkyl/arylated quinoxalines. Direct arylation on the quinoxaline ring induced puckering of the quinoxaline bifused ring to the discontinued conjugation ring system, resulting in pseudotetrahedral geometry around the 2-position of quinoxalines. This, in turn, forms two dissimilar nitrogen environments in a single molecule, one with an electron-donating sp^3-site and the other with an electron-accepting sp^2-site. As a result of the increased charge transfer character, culminated by strong ICT effects, the UV and PL spectra of 2-alkyl/arylated quinoxaline compounds was progressively red-shifted compared to the quinoxaline ligand (**1**) with dramatic enhancement of PL efficiency (40−60%). The HOMO and LUMO energy levels determined by CVs and DFT calculation were higher than those of the quinoxaline ligand, showing the increased donor character and decreased acceptor character of 2-alkylated compounds. This method offers a powerful tool for the preparation of highly emissive electroluminescent materials using a quinoxaline moiety.

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Supporting Information Available: Experimental details and characterization data, CIF, related optical data, CVs, and calculation data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) (a) Delley, B. *J. Chem. Phys.* **1990**, *92*, 508. (b) Delley, B. *J. Chem. Phys.* **2000**, *113*, 7756.

(20) Kulkarni, A. P.; Wu, P.-T.; Kwon, T. W.; Jenekhe, S. A. *J. Phys. Chem. B* **2005**, *109*, 19584.