Conformation impact on spectral properties of bis(5,7-dimethyl-1,8-naphthyridin-2-yl)amine and its Zn^{II} complex†

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Received (in Montpellier, France) 4th April 2007, Accepted 5th June 2007
First published as an Advance Article on the web 28th June 2007
DOI: 10.1039/b705149b

Novel dual fluorescent compounds, bis(5,7-dimethyl-1,8-naphthyridin-2-yl)amine and its Zn^{II} complex, were synthesized and crystallographically characterized; their dual fluorescence and two groups of well-structured absorption bands in CH_2Cl_2 were attributed to a molecular conformational equilibrium.

Introduction

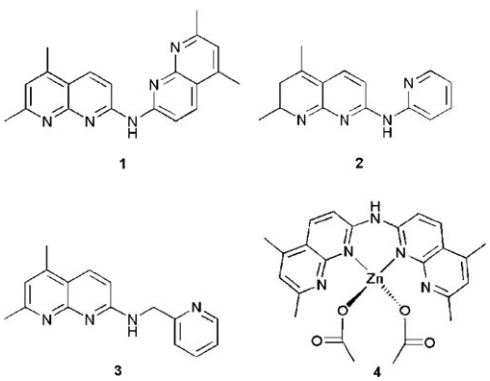
Dual fluorescence from organic molecules has been actively investigated in the past few decades.[1] Generally, such phenomena result from the formation of an inter- or intramolecular excited complex[2–5] (excimer, exciplex, and so forth), a change of structure involving ground state or excited state proton transfer,[6–9] or intramolecular charge transfer.[10–17] The most frequently studied types of dual fluorescence involve twisted intramolecular charge transfer (TICT)[11–14] or planar intramolecular charge transfer (PICT)[15–17] excited state emission. Much attention has also been paid to dual fluorescence from ground state structural changes.[18] Previously, Dey and Warner supposed that dual fluorescence in 9-(*N*,*N*-dimethylamino)anthracene (9-DMA) originated from the existence of a conformation equilibrium in both the ground and excited states.[19] Unfortunately, the absorption spectrum of 9-DMA didn't exhibit a marked red-shifted long wavelength band. To develop a better understanding of the correlation between photophysical properties and molecular conformation, we are interested in designing new molecular systems that can display obvious dual emission and absorption.

In the present study, the synthesis and photophysical properties of bis(5,7-dimethyl-1,8-naphthyridin-2-yl)amine (**1**) are reported. It was found that this compound shows both dual fluorescence and two groups of well-structured absorption bands. Comparison investigations on the photophysical properties of compound **1** and two reference compounds (2-(2-pyridyl)amino-5,7-dimethyl-1,8-naphthyridine (**2**) and 2-[*N*-(2-pyridyl)methyl]amino-5,7-dimethyl-1,8-naphthyridine (**3**) (Scheme 1)), as well as the Zn^{II} complex of **1** (**4**), have shown that an electronic interaction between the NH group and two naphthyridine ring systems is responsible for the dual emission and red-shifted absorption bands.

Results and discussion

Compound **1** (Fig. 1) has a near planar geometry, and the dihedral angle between the two naphthyridine ring planes is only 15.5°. The bond lengths of N(3)–C(9) and N(3)–C(11) are 1.387 and 1.391 Å, respectively, and are partially double bond in character. This suggests the presence of electronic coupling between the NH group and the two naphthyridine ring systems. However, this type of interaction is likely to be weakened in solution; the lone electron pair of the NH group is sensitive to its environment and readily interacts with protons. In solution, the free rotation of the two naphthyridine rings around C–N bonds would impact on the electronic coupling, resulting in an intramolecular conformational equilibrium between near planar and twisted conformations in the ground state. In particular, in protic solvents, due to the interaction between solvent protons and the lone electron pair of the NH group, the conjugation would be completely broken, and the twisted conformation would be prominent, causing the lone electron pair orbital to be out of the plane of the p-orbitals of the naphthyridine rings.

The absorption spectrum of compound **1** consists of two structured absorption bands, the relative intensities of which are obviously correlated with properties of the solvent (Fig. 2). In a weak polar solvent, *e.g.* toluene, the two absorption bands are of comparable intensity, while in an aprotic solvent, *e.g.* CH_2Cl_2, the low energy absorption bands, ranging from 390–475 nm, decreased, but with a concomitant development of the high energy absorption bands in the region 300–390 nm.



Scheme 1

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† Electronic supplementary information (ESI) available: Figures S1–S7. See DOI: 10.1039/b705149b

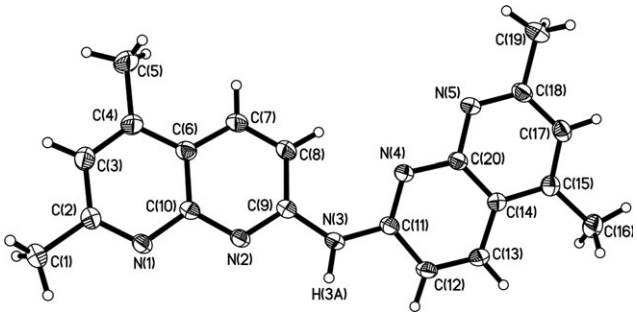

Fig. 1 Perspective view of **1** with 30% probability ellipsoids. Selected bond lengths (Å) and angles (°): N(1)–C(2) 1.325(2), N(1)–C(10) 1.367(2), N(2)–C(10) 1.358(2), N(2)–C(9) 1.327(2), N(3)–C(9) 1.387(2), N(3)–C(11) 1.391(2), C(9)–N(3)–C(11) 130.72(1), C(9)–N(3)–H(3A) 113.4(1), C(11)–N(3)–H(3A) 115.7(1).

With the NH group protonated, the low energy absorption bands disappeared. Addition of CH_3OH to the CH_2Cl_2 solution of compound **1** afforded an absorption spectra with an isosbestic point at 390 nm, weakened low energy absorption bands and an accompanying increase in the high energy absorption intensity (Fig. 2). The solution colour changed from yellow to colorless. On the basis of structural analysis, we assume that absorption in the longer wavelength region is associated with a near planar conformation of **1**, while the absorption at the shorter wavelength involves the twisted conformation.

To verify this tentative assignment, two reference compounds, **2** and **3**, were synthesized (Scheme 1). In **2**, the interaction between the naphthyridine ring and pyridine ring system was similar to that in **1**, however, the same interaction is unlikely in **3** because of the introduction of a methylene group. In accordance with its structure, it was expected that the absorption spectra of **2** would display a similar solvent effect to that of compound **1** (Fig. S1†). Indeed, an investigation of its absorption spectra revealed that there is weak absorption in the long wavelength region in aprotic solvents, indicating the presence of a weak interaction between the naphthyridine and pyridine rings, while in protic solvents, long wavelength absorption disappeared. As expected, long wavelength absorption by compound **3** has not been observed, both in protic and aprotic solvents (Fig. S2†).

It is foreseeable that when rotation of the naphthyridine ring around the C–N bond is totally prevented, **1** should mostly display long wavelength absorption bands in aprotic solvents. Complex **4** affords a chance for us to observe such phenomena, where **1** acts as a bidentate ligand, its two naphthyridine rings being fixed by means of coordination to the photo-inert metal center Zn^{II}. The structural investigation of **4** by X-ray crystallography shows that the molecule has a rigid planar geometry, and the dihedral angle between the two naphthyridine ring planes is less than 5° (Fig. 3). The long wavelength absorption of **4** is prominent, both in CH_3CN and CH_2Cl_2 solutions (Fig. S3†). On the contrary, the long wavelength absorption of complex **4** is fairly weak in CH_3OH compared to those in CH_2Cl_2 or CH_3CN due to interaction between protic solvents and the lone electron pair, but is stronger than that of free ligand **1** in CH_3OH solution. To obtain more information, acid titration experiments on complex **4** were performed (Fig. S4†). When HBF_4 (3.5×10^{-3} mol L^{-1} in CH_3CN) was added to a CH_3CN solution of complex **4**, the long wavelength absorption completely disappeared. Therefore, the data obtained in the present study shows that the absorption in the long wavelength region is associated with electronic excitations, in which both the two naphthyrine ring systems and the lone electron pair of the NH group participate, and the absorption at a shorter wavelength involves only electronic excitations centered within one naphthyridine ring system.

The solvent effect on the fluorescence of compound **1** was in accordance with that observed in its absorption spectra (Fig. 4). In protic solvent CH_3OH, compound **1** showed fluorescence emission only in the short wavelength region, while in CH_2Cl_2, it displayed two groups of emission bands that were excitation wavelength-dependent. Upon excitation at 355 nm, **1** displayed a fluorescence emission at around 380 nm with a tail extending up to more than 500 nm. In the case of excitation at 420 nm, a longer wavelength emission band (λ_{max} = 478 nm) developed in the region 450–600 nm. Though

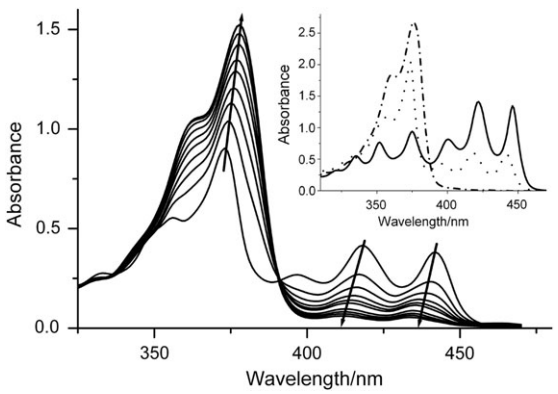

Fig. 2 Absorption spectra changes of compound **1** in CH_2Cl_2 at room temperature upon addition of CH_3OH. Insert: Absorption spectra of compound **1** (50 μM) in toluene (solid line), CH_2Cl_2 (dotted line) and CH_3OH (dash–dot line) at room temperature.

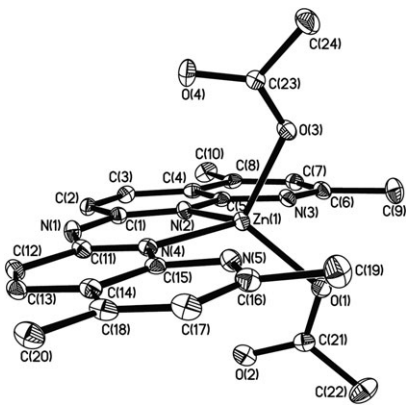

Fig. 3 Perspective view of **4** with 30% probability ellipsoids; all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Zn(1)–O(1) 1.947(3), Zn(1)–O(3) 1.961(3), Zn(1)–N(2) 2.068(3), Zn(1)–N(4) 2.048(3), N(4)–Zn(1)–N(2) 89.71(1), O(1)–Zn(1)–O(3) 103.50(1).

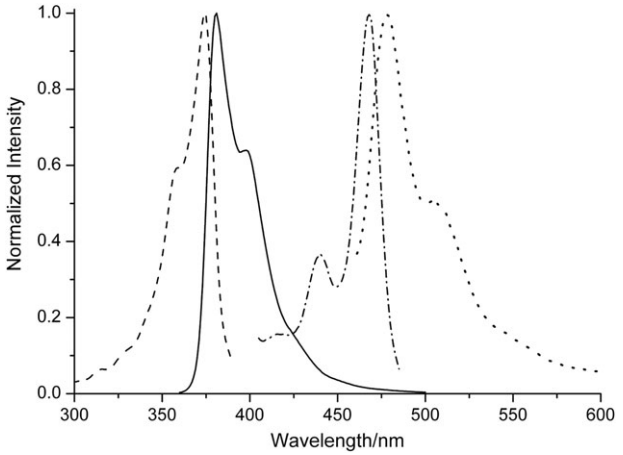

Fig. 4 Normalized emission and excitation spectra of **1** in CH_2Cl_2 at room temperature. Solid line: emission (λ_{ex} = 355 nm); dashed line: excitation (λ_{em} = 400 nm); dotted line: emission (λ_{ex} = 420 nm); dash–dot line: excitation (λ_{em} = 506 nm).

the shapes of the fluorescence excitation spectra of the corresponding emission bands are similar, the excitation energies are completely different to each other. The excitation spectrum corresponding to the high energy emission at 400 nm in CH_2Cl_2 was identical to its short wavelength absorption band, whereas the excitation spectrum of the low energy emission at 506 nm was markedly red-shifted with respect to that of compound **1** (Fig. 4). The excitation spectra were measured with various concentrations of **1** (Fig. S5†), from which there was no detectable change in the excitation energy at 467 nm, except for the decrease in intensity of the excitation spectra. We tentatively suggest that dual fluorescence originates from two excited states. The small Stokes shift suggests that the excited state employs a molecular structure similar to that of the ground state.

Complex **4** also exhibits dual fluorescence emission. At room temperature, two groups of emission bands with a vibronic structure are evident in CH_2Cl_2, and the low energy emission is prominent, while the high energy emission dominates in CH_3OH (Fig. 5). Furthermore, with the addition of acid (HBF_4), the nitrogen atom of the protonated NH group results in the quenching of the low energy emission and the enhancement of high energy emission (Fig. 5). The above results further support the notion that a lone electron pair interaction with the naphthyridine ring system plays a key role in the red-shifting of the low energy absorption bands.

In summary, a dual fluorescent compound, bis(5,7-dimethyl-1,8-naphthyridin-2-yl)amine, has been synthesized and its spectroscopic properties investigated. This compound shows two groups of absorption due to the conformational equilibrium between a near planar molecular geometry and a twisted geometry. The excitation spectra of the two fluorescence bands are different from each other and resemble the two absorption bands, respectively, which suggests that dual fluorescence of compound **1** comes from different excited states of the two different conformations in the ground state. Spectral investigations on its Zn^{II} complex and reference compounds **2** and **3** afforded further evidence for the mechanism of dual fluorescence and absorption.

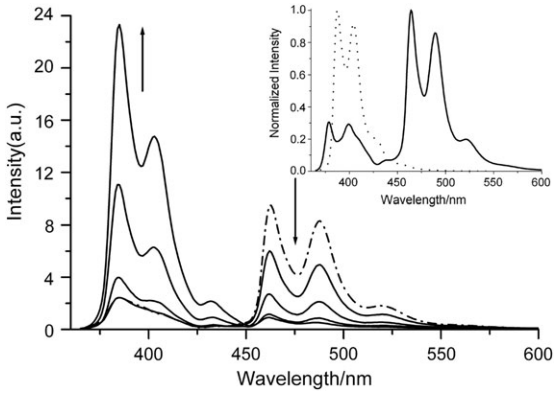

Fig. 5 Spectrofluorimetric titration of HBF_4 to a CH_3CN solution of **4** (dash–dot line: [HBF_4] = 0). Arrows indicate changes in the intensities of bands upon acidification. Insert: Normalized emission spectrum of **4** in CH_2Cl_2 (solid line) and CH_3OH (dotted line) at room temperature (λ_{ex} = 360 nm).

Experimental

General methods

UV-vis absorption spectra were recorded using a Hitachi U-3010 spectrophotometer. Emission and excitation spectra were obtained using a Hitachi F-4500 fluorescence spectrofluorimeter. ^{1}H NMR spectra were measured on a Bruker Avance DPX-400 MHz resonance spectrometer using TMS ($SiMe_4$) as an internal reference at room temperature.

Syntheses

General procedure for the synthesis of **1–3**.[21,22] A suspension of 2,4-dimethyl-7-chloro-1,8-naphthyridine,[23,24] amine and powdered KOH in a 2 : 2 : 3 molar ratio in toluene was refluxed for 24 h. Upon removal of the solvent, the residue was washed with water until the washings were neutral. The product was purified by column chromatography over a silica gel column using $CHCl_3/CH_3CH_2OH$ as the eluent.

1: The amine is 2,4-dimethyl-7-amino-1,8-naphthyridine.[25] Yield 0.72 g, 22%; ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ = 2.60 (s, 6 H, CH_3), 2.62 (s, 6 H, CH_3), 7.17 (s, 2 H), 8.28 (d, J = 9.0 Hz, 2 H), 8.45 (d, J = 9.0 Hz, 2 H) and 10.68 (s, 1 H); MS(EI): m/z = 330 (M + 1), 329 and 328 (M − 1) (100%).

2: The amine is 2-aminopyridine. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ = 2.60 (s, 3 H, CH_3), 2.70 (s, 3 H, CH_3), 6.95 (t, J = 6.7 Hz, 1 H), 7.02 (s, 1 H), 7.42 (d, J = 8.8 Hz, 1 H), 7.73 (t, J = 7.8 Hz, 1 H), 8.14 (d, J = 8.9 Hz, 1 H), 8.33 (d, J = 4.2 Hz, 1 H), 8.42 (s, 1 H) and 10.90 (s, 1 H).

3: The amine is 2-aminomethylpyridine. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ = 2.52 (s, 3 H, CH_3), 2.64 (s, 3 H, CH_3), 4.98 (d, J = 4.4 Hz, 2 H), 6.30 (s, 1 H), 6.74 (d, J = 8.9 Hz, 1 H), 6.87 (s, 1 H), 7.18 (t, J = 6.1 Hz, 1 H), 7.34 (d, J = 7.8 Hz, 1 H), 7.64 (t, J = 7.6 Hz, 1 H), 7.93 (d, J = 8.9 Hz, 1 H) and 8.56 (d, J = 4.6 Hz, 1H).

4: A CH_3OH solution (10 mL) of $Zn(OAc)_2 \cdot 2H_2O$ (0.13 mg, 0.60 mmol) was added to a CH_2Cl_2 solution (20 mL) of **1** (0.20 mg, 0.60 mmol). The yellow solution was stirred for 5 h at room temperature and then filtered. Crystals of **4** $\cdot CH_2Cl_2$ suitable for X-ray structural analysis were obtained by vapor

diffusion of diethyl ether into the filtrate. Yield 0.25 g, 80%; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ = 2.10 (s, 6 H, CH_3), 2.11 (s, 6 H, CH_3), 2.50 (s, 6 H, CH_3), 6.82 (s, 2 H), 8.24 (d, J = 9.1 Hz, 2 H) and 8.31 (d, J = 9.1 Hz, 2 H).

X-Ray crystallography

Crystals of **1** and **4** suitable for X-ray structure analysis were grown from a CH_2Cl_2/CH_3OH mixed solution by the slow diffusion of diethyl ether over a period of several days. The crystal structure of **4** was of its dichloromethane solvate. The diffraction data were collected with graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å) on a Rigaku R-AXIS RAPID IP X-ray diffractometer. An absorption correction was applied by the correction of symmetry-equivalent reflections using the ABSCOR program. The structure was solved by direct methods using the SHELXS-97 program and refined by full matrix least-squares on F^2 using SHELXL-97 software.[20] The hydrogen atoms were added using ideal geometries, except for H3A in **1** and H1 in **4**·CH_2Cl_2. The N3–H3A and N1–H1 bond lengths were restrained, with the DFIX parameters being (0.90, 0.01) and (0.86, 0.01), respectively (Fig. S6 and S7†).

Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications. CCDC 635917 (**1**) and CCDC 635918 (**4**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b705149b

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20671094, 20471066). We are grateful to the State Key Project (2005CCA06800) for financial support. We thank foundation (50418010) for NSFC/RGC Joint Research.

References

1 Z. R. Grabowski, K. Rotkiewicz and W. Rettig, *Chem. Rev.*, 2003, **103**, 3899.
2 R. V. Todesco, R. A. Basheer and P. V. Kamat, *Macromolecules*, 1986, **19**, 2390.
3 S. A. Jenekhe, L. Lu and M. M. Alam, *Macromolecules*, 2001, **34**, 7315.
4 Y. Shiraishi, Y. Tokitoh, G. Nishimura and T. Hirai, *Org. Lett.*, 2005, **7**, 2611.
5 N. Chandrasekharan and L. A. Kelly, *J. Am. Chem. Soc.*, 2001, **123**, 9898.
6 S. Santra, G. Krishnamoorthy and S. K. Dogra, *J. Phys. Chem. A*, 2000, **104**, 476.
7 L. M. Tolbert and K. M. Solntsev, *Acc. Chem. Res.*, 2002, **35**, 19.
8 J. Waluk, *Acc. Chem. Res.*, 2003, **36**, 832.
9 O. H. Kwon, Y. S. Lee, B. K. Yoo and D. J. Jang, *Angew. Chem., Int. Ed.*, 2006, **45**, 415.
10 J. S. Yang, Y. D. Lin, Y. H. Chang and S. S. Wang, *J. Org. Chem.*, 2005, **70**, 6066.
11 K. Rotkiewicz, K. H. Grellmann and Z. R. Grabowski, *Chem. Phys. Lett.*, 1973, **19**, 315.
12 D. Rappoport and F. Furche, *J. Am. Chem. Soc.*, 2004, **126**, 1277.
13 I. Gómez, M. Reguero, M. Boggio-Pasqua and M. A. Robb, *J. Am. Chem. Soc.*, 2005, **127**, 7119.
14 S. Murali and W. Rettig, *J. Phys. Chem. A*, 2006, **110**, 28.
15 K. A. Zachariasse, S. I. Druzhinin, W. Bosch and R. Machinek, *J. Am. Chem. Soc.*, 2004, **126**, 1705.
16 T. Yoshihara, S. I. Druzhinin and K. A. Zachariasse, *J. Am. Chem. Soc.*, 2004, **126**, 8535.
17 S. Cogan, S. Zilberg and Y. Haas, *J. Am. Chem. Soc.*, 2006, **128**, 3335.
18 G. Bartocci, A. Spalletti and U. Mazzucato, in *Conformational Analysis of Molecules in Excited States*, ed. J. Waluk, Wiley-VCH, New York, 2000, ch. 5, pp. 237.
19 J. Dey and I. M. Warner, *J. Phys. Chem. A*, 1997, **101**, 4872.
20 G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
21 K. Y. Ho, W. Y. Yu, K. K. Cheung and C. M. Che, *J. Chem. Soc., Dalton Trans.*, 1999, 1581.
22 J. L. Zuo, W. F. Fu, C. M. Che and K. K. Cheung, *Eur. J. Inorg. Chem.*, 2003, 255.
23 E. V. Brow, *J. Org. Chem.*, 1965, **30**, 1607.
24 G. R. Newkome, S. J. Garbis, V. K. Majestic, F. R. Fronczek and G. Chiari, *J. Org. Chem.*, 1981, **46**, 833.
25 R. A. Henry and P. R. Hammond, *J. Heterocycl. Chem.*, 1977, **14**, 1109.

