Intense one- and two-photon excited fluorescent bis(BF_2) core complex containing 1,8-naphthyridine derivative

Supporting Information

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Experimental

Materials and methods

General methods: 1H NMR spectra were measured on Bruker DPX-400 (400 MHz) at 299 K with chemical shifts (δ, ppm) relative to tetramethylsilane (Me_4Si) for 1H. Elemental analysis was carried out with a Carlo Erba 1106 element analysis instrument. ESI-MS data were recorded by APEXII Model FT-ICR mass spectrograph. All chemicals for the synthesis were purchased from commercial suppliers and solvents (HPLC) were purified according to standard procedures.

Spectroscopic measurements: The UV-Vis spectra were taken on a HITACHI U-3010 spectrophotometer, and the corrected emission spectra of solutions and solids were carried out with a HITACHI F-4500 fluorescence spectrophotometer adapted to a right-angle configuration at room temperature. Fluorescein in 0.1 N NaOH (Φ_f = 0.9) was used as reference system.

Experimental procedure for X-ray crystallographic analysis: Crystal of complex **1** suitable for X-ray structure analysis was obtained by slow evaporation of *n*-pentane into a solution of complex **1** in dichloromethane. The diffraction data were collected on a Rigaku R-AXIS RAPID IP X-Ray diffractometer using a graphite monochromator with Mo-Kα radiation (λ = 0.071073 nm) at 113 K. The structure was solved by direct methods and refined by full-matrix least-squares methods on all F^2 data (SHELX-97).[1]

Measurements of two-photon absorption and two-photon excited fluorescence: Two-photon absorption (TPA) and two-photon excited fluorescence (TPEF) spectra of complex **1** were recorded on a SD2000 spectrometer (Ocean Optical) with the excitation by a mode-locked Ti-sapphire femtosecond laser (Tsunami, Spectra-physics) for which the oscillating wavelength, pulse width and repetition rate were 780 nm, 80 fs and 82 MHz, respectively.

Molecular orbital calculation details: The calculation for **1** was based on the time-dependent density functional theory (TD-DFT) and performed at the B3LYP/6-311+G*(TD-DFT, 50-50) level, employing the Gaussian 03 suit of programs.[2] Geometric data from X-ray diffraction analysis were used as the initial parameters for the calculation.

Synthetic procedure

The compounds (E)-1,2-bis(5,7-dimethyl-1,8-naphthyridin-2-yl)diazene (**4**) and 1,2-bis(5,7-dimethyl-1,8-naphthyridin-2-yl)hydrazine (**5**) were synthesized in good yields and reported by our group.[3]

Synthesis and characterization of the bis(BF2) core complex 1: $BF_3{\cdot}Et_2O$ (4 mL) was added dropwise to an ice-cooled solution of 2,6-Lutidine (2 mL) and 5 (0.15 g, 0.43 mmol) in Et_2O (100 mL) with stirring for half an hour under a nitrogen atmosphere. After the mixture was stirred in the ice bath for 5 hours, the reaction was quenched by adding of a saturated aqueous solution of $NaHCO_3$ (50 mL). The aqueous layer was extracted with Et_2O (3×100 mL), then the combined organic layers were washed by water for three times and dried over $MgSO_4$. After filtration and removal of the solvent under reduced pressure, the crude product was purified by chromatography on silica gel (200-300 mesh), using $CHCl_3$ as eluent to give the pure product as bright yellow powder. Yield: 40% ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si) δ 2.60 (s, 3H, 4-Me of naphthyridyl rings), 2.70 (s, 3H, 2-Me of naphthyridyl rings), 7.06 (s, 1H, naphthyridyl proton), 7.16 (d, J = 9.1 Hz, 1H, naphthyridyl proton), 8.16 (d, J = 9.3 Hz, 1H, naphthyridyl proton); Anal. Calc. for $C_{20}H_{18}B_2F_4N_6$: C, 54.59; H, 4.12; N, 19.10. Found: C, 54.36; H, 4.22; N, 19.34%. TOF MS (EI) *m/z*: 440.

(1) Sheldrick, G. M. *SHELX-97, Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, **1997**.

(2)Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, Jr., T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. Gaussian 03, Revision C.02, Gaussian, Inc.: Wallingford CT, **2004**.

(3) Fu, W. –F.;. Li, H. F. –J.; Wang, D. -H.; Zhou, L. -J.; Li, L.; Gan, X.; Xu, Q. -Q.; Song, H. -B. *Chem. Commun*. **2009,** 5524.

Results

Table S1. Summary of X-ray crystallographic data for complex **1.**.

compound	**1**
formula	$C_{20}H_{18}B_2F_4N_6$
fw	440.02
space group	Pbca
cryst syst	Orthorhombic
a(Å)	8.538(2)
b(Å)	14.696(3)
c(Å)	15.467(3)
α (deg)	90
β (deg)	90
γ (deg)	90
V(Å^3)	1940.6(7)
Z	4
T (K)	113(2)
ρ_{calcd}(g cm^{-3})	1.506
θ rang (deg)	3.06-27.51
μ (mm^{-1})	0.119
crystal size (mm)	0.10×0.08×0.06
GOF	1.068
no. of unique data	2221
no. of parameters	148
R_{int}	0.0578
R_1[a]	0.0453
wR_2[a]	0.1153
max, min peaks (e Å^{-3})	0.320, -0.241

[a] $I>2\sigma(I)$. $R_1 = \Sigma||F_o| - |F_c||\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

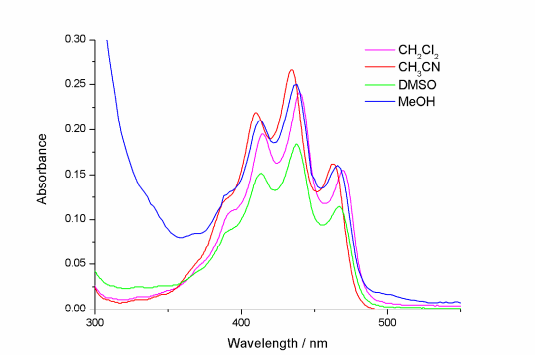


Figure S1. UV-Vis absorption spectra of complex **1** in different solvent at 298 K.

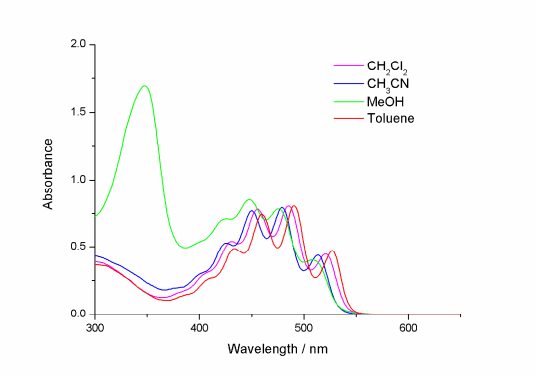


Figure S2. UV-Vis absorption spectra of Compound **5** in different solvent at 298 K.

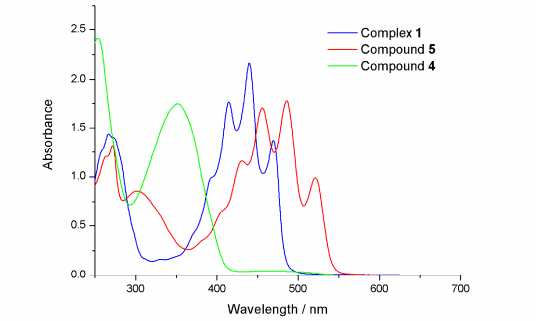


Figure S3. UV-Vis absorption spectra of compounds **1**, **4** and **5** in dichloromethane at 298 K.

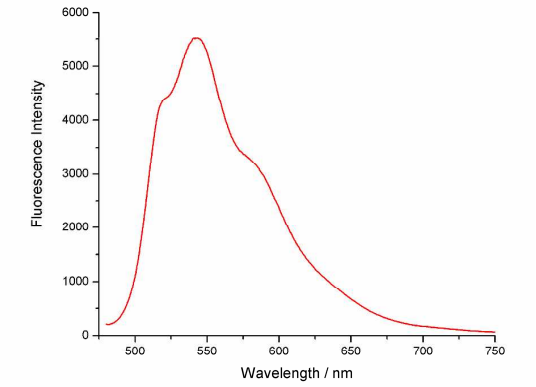


Figure S4. Fluorescence emission spectrum of complex **1** in solid state.

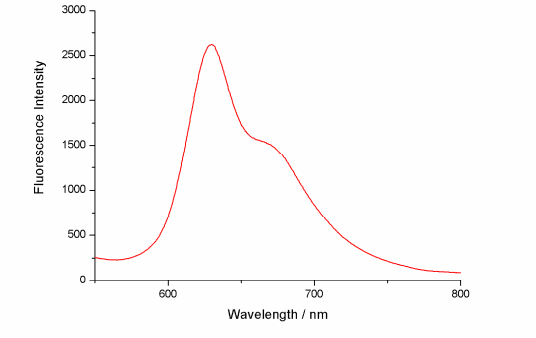


Figure S5. Fluorescence emission spectrum of compound **5** in solid state.

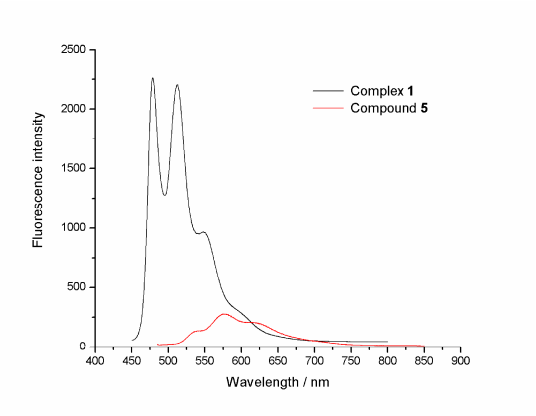
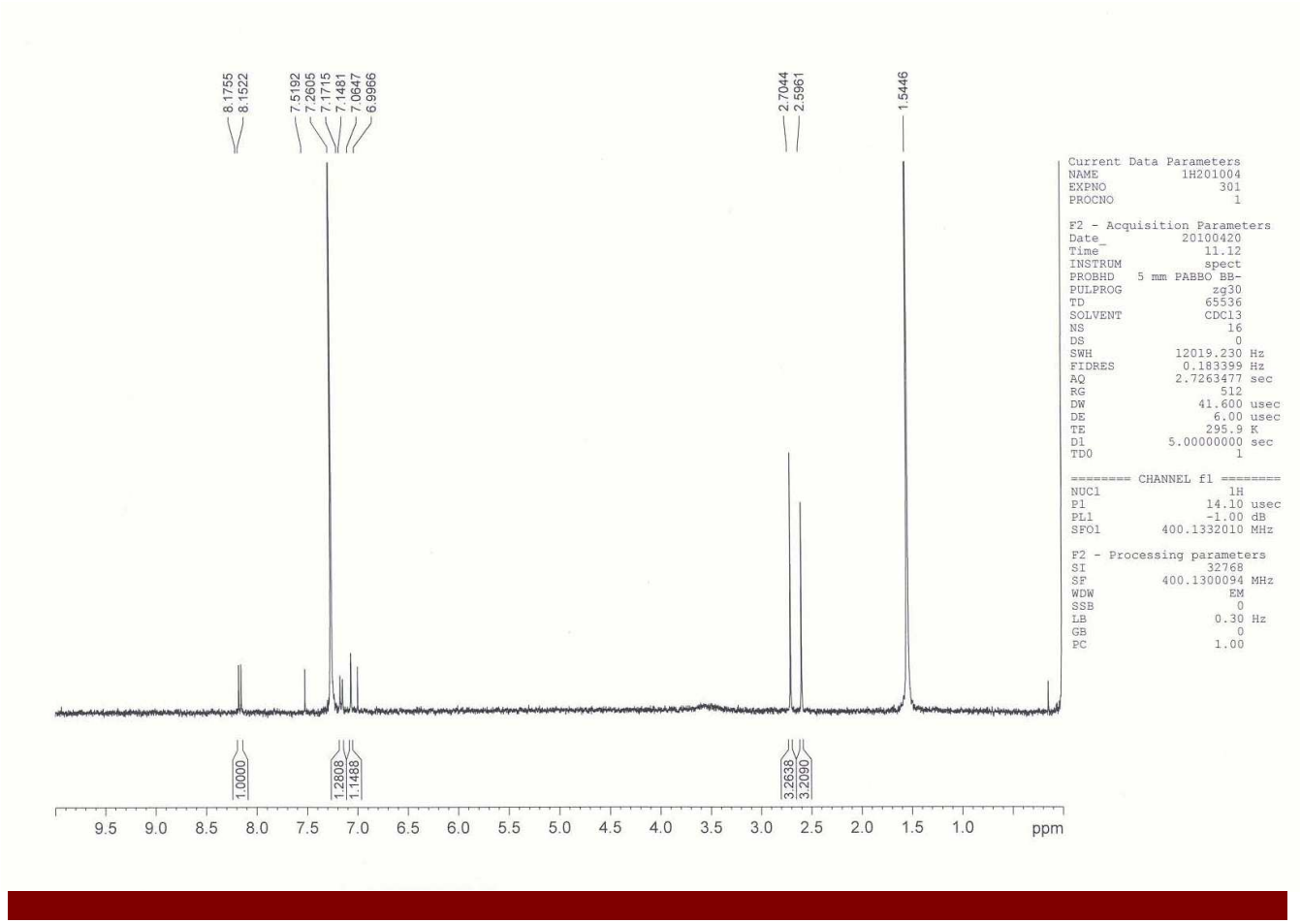


Figure S6. Fluorescence emission spectra of compounds **1** and **5** in dichloromethane at 298 K.

^{1}H NMR Spectrum of **1**



TOF MS (EI) Spectrum of **1**