# Copper(I) complex with BINAP and 3,5-dimethylpyrazole: synthesis and photoluminescent properties

**Aleksei A. Titov, Oleg A. Filippov, Alexander F. Smol'yakov, Alexey A. Averin and Elena S. Shubina**

**Materials and methods.**

All manipulations were performed under argon atmosphere. Solvents (acetone, acetonitrile, hexane, DCM) were dried by standard procedures and distilled prior to use.

$^1$H, $^{19}$F and $^{31}$P NMR spectra were recorded on a Bruker Avance 400 spectrometer. The photoluminescence spectra and lifetime measurements of the phosphorescence were recorded at 77K and 298K using a Fluorolog-3 spectrofluorometer system (HORIBA Jobin–Yvon) (the excitation source was a 450 W Xenon lamp equipped with Czerny–Turner double monochromators, the registration channels were a R928 photomultiplier, while 150 W pulsed Xenon lamp was used for the life time measurements). The powders for these measurements were packed in quartz capillaries. The phosphorescence quenching curves were analyzed using the FluoroEssenceTM software for the calculation of phosphorescence lifetime values.

**Synthetic procedure.**

The solution of BINAP (98.4 mg, 0.158 mmol) in MeCN (2 ml) was added to the solution of [Cu(MeCN)$_4$]BF$_4$ (50 mg, 0.158 mmol) and 3,5-dimethylpyrazole (15.2 mg, 0.158 mmol) in acetone (3 ml). The reaction mixture was stirred overnight at room temperature, and the precipitate formed was filtered off. The remaining residue was washed with acetone (5 ml) and dissolved in CH$_2$Cl$_2$ (3 ml). Hexane (10 ml) was added to the solution, and the off-white product was isolated by filtration, washed with ether and dried *in vacuo* yielding the desired product (121.4 mg, 88%).

**Characteristics of the obtained complex.**

$^1$H NMR (CD$_2$Cl$_2$), $\delta$: 2.25 (s, CH$_3^{Pz}$, 6H), 6.04 (br. s, CH$^{Pz}$, 1H), 6.60–7.88 (m, 32H$^{BINAP}$), 11.31 (br. s, NH$^{Pz}$, 1H). $^{31}$P{$^1$H} NMR (CD$_2$Cl$_2$), $\delta$: –0.01. $^{19}$F NMR (CD$_2$Cl$_2$), $\delta$: –152.9. Elemental Analysis for C$_{49}$H$_{40}$CuN$_2$P$_2$BF$_4$, Anal/Calc: C, 67.83/67.71; H, 4.75/4.64; N, 3.19/3.22; P, 7.02/7.13

**X-ray diffraction study.**

Single crystal X-ray diffraction experiments were carried out using a Bruker SMART APEX II diffractometer (graphite monochromated Mo-K$_\alpha$ radiation, $\lambda$ = 0.71073 Å, $\omega$-scan technique). The APEX II software [S1] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction. All the calculations (space group and structure determination, refinements, graphics, and structure reporting) were made using the SHELXL2014[S2] and OLEX2[S3] program packages. Experimental details and crystal parameters are listed in Table S1. The structures were solved by direct methods and refined by the full-matrix least-squares technique against $F^2$ with the anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed geometrically and included in the structure factors calculations in the riding motion approximation.

**Table S1** Crystal data, data acquisition, and structure refinement parameters for **1**.

| Compound | **1** |
|---|---|
| Molecular formula | C$_{49}$H$_{40}$BCuF$_4$N$_2$ P$_2$ |
| Formula weight | 869.12 |
| Dimension, mm | 0.33×0.27×0.19 |
| Temperature, K | 120(2) |
| Crystal system | monoclinic |
| Space group | $C$/c |
| $a$/Å | 20.3340(7) |
| $b$/Å | 14.9605(5) |
| $c$/Å | 14.4148(5) |
| $\alpha$/deg | 90 |
| $\beta$/deg | 109.7790(10)°, |
| $\gamma$/deg | 90 |

| | | |
|---|---|---|
| $V/\text{Å}^3$ | | 4126.4(2) |
| $Z$ | | 4 |
| $\rho_{calc}/\text{g cm}^{-3}$ | | 1.399 |
| Linear absorption $(\mu)/\text{mm}^{-1}$ | | 0.663 |
| $T_{min}/T_{max}$ | | 0.6557/0.7461 |
| $2\theta_{max}/\text{deg}$ | | 30.58 |
| No. unique refl. $(R_{int})$ | | 45327 (0.0215) |
| No. observed refl. $(I>2\sigma(I))$ | | 11845 |
| No. parameters | | 534 |
| $R_1$ (on $F$ for observed refl.)[a] | | 0.0263 |
| $wR_2$ (on $F^2$ for all refl.)[b] | | 0.0674 |
| GOOF | | 1.035 |

[a] $R_1 = \Sigma\left|\left|F_o\right| - \left|F_c\right|\right|/\Sigma\left|F_o\right|$

[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2\}^{1/2}$

**Computation details.**

The structure of complex **1** was optimized without any restrictions by the Gaussian 09[S4] software using PBE0[S5] functional and def2-SVP[S6] basis set. TD-DFT calculations were provided on the same level of theory.

**Table S2** Impacts of atomic fragments to the hole (ground state) and electron (excited state) of $S_0 \rightarrow S_n$ transitions.

| | $S_1$ (391 nm, $f = 0.039$) | | $S_2$ (354 nm, $f = 0.021$) | |
|---|---|---|---|---|
| | hole | electron | hole | electron |
| Cu | 42.1 | 2.3 | 39.9 | 1.1 |
| Pz | 6.7 | 0.7 | 6.3 | 0.2 |
| $BF_4$ | 0.4 | 0.2 | 0.4 | 0.1 |
| 2P | 30.8 | 7.7 | 30.7 | 4.2 |
| binaph+4Ph | 20.2 | 89.2 | 22.7 | 94.4 |

| | BINAP[a] | 50.9 | 96.8 | 53.4 | 98.7 |
|---|---|---|---|---|---|

| | S₃ (339 nm, $f = 0.019$) | | S₄ (326 nm, $f = 0.009$) | |
|---|---|---|---|---|
| | hole | electron | hole | electron |
| Cu | 19.4 | 1.8 | 42.1 | 0.2 |
| Pz | 2.6 | 0.4 | 7.0 | 0.3 |
| BF₄ | 0.2 | 0.1 | 0.3 | 0.0 |
| 2P | 6.7 | 5.9 | 32.1 | 7.5 |
| binaph+4Ph | 71.2 | 91.7 | 18.5 | 92.1 |
| BINAP[a] | 77.8 | 97.7 | 50.6 | 99.6 |

| | S₅(322 nm, $f = 0.005$) | | S₆(313 nm, $f = 0.013$) | |
|---|---|---|---|---|
| | hole | electron | hole | electron |
| Cu | 40.9 | 0.9 | 18.7 | 1.8 |
| Pz | 6.5 | 0.1 | 2.3 | 0.4 |
| BF₄ | 0.4 | 0.0 | 0.1 | 0.1 |
| 2P | 31.9 | 11.5 | 5.5 | 5.8 |
| binaph+4Ph | 20.3 | 87.5 | 73.4 | 92.0 |
| BINAP[a] | 52.2 | 99.0 | 78.8 | 97.8 |

[a] Impact of BINAP ligand is a sum of organic part and P atoms.

**Table S3** XYZ coordinates of optimized complex **1**.

| | | | |
|---|---|---|---|
| 29 | -1.495457000 | 0.202907000 | -0.562948000 |
| 15 | 0.141844000 | 1.806908000 | -0.424762000 |
| 15 | -0.230416000 | -1.704566000 | -0.229636000 |
| 9 | -2.420752000 | -0.089019000 | 1.502163000 |
| 9 | -4.579189000 | -0.238222000 | 2.190122000 |
| 9 | -3.023774000 | 0.802172000 | 3.526623000 |
| 9 | -2.953357000 | -1.474016000 | 3.251167000 |
| 7 | -3.362725000 | 0.320749000 | -1.321317000 |
| 7 | -4.429699000 | 0.224675000 | -0.524940000 |

| | | | |
|---|---|---|---|
| 1 | -4.323787000 | 0.105305000 | 0.493211000 |
| 6 | -3.832349000 | 0.446566000 | -2.566593000 |
| 6 | -2.909974000 | 0.545658000 | -3.732428000 |
| 1 | -1.903206000 | 0.838047000 | -3.400485000 |
| 1 | -3.263448000 | 1.289843000 | -4.460610000 |
| 1 | -2.828096000 | -0.419375000 | -4.258556000 |
| 6 | -6.899963000 | 0.207193000 | -0.507677000 |
| 1 | -7.533168000 | -0.578278000 | -0.945543000 |
| 1 | -7.448302000 | 1.158444000 | -0.586589000 |
| 1 | -6.753536000 | -0.015956000 | 0.558187000 |
| 6 | -5.239752000 | 0.432587000 | -2.543827000 |
| 1 | -5.915365000 | 0.515234000 | -3.391866000 |
| 6 | -5.586932000 | 0.285549000 | -1.204890000 |
| 6 | 0.907168000 | -1.194979000 | 1.127454000 |
| 6 | 0.488468000 | -1.511580000 | 2.449366000 |
| 1 | -0.426534000 | -2.086793000 | 2.602453000 |
| 6 | 1.194824000 | -1.070788000 | 3.538109000 |
| 1 | 0.849167000 | -1.315620000 | 4.545496000 |
| 6 | 2.368396000 | -0.295324000 | 3.378781000 |
| 6 | 3.132725000 | 0.131814000 | 4.494993000 |
| 1 | 2.798067000 | -0.155083000 | 5.495306000 |
| 6 | 4.269777000 | 0.885677000 | 4.326527000 |
| 1 | 4.853895000 | 1.203046000 | 5.193745000 |
| 6 | 4.680537000 | 1.254612000 | 3.026500000 |
| 1 | 5.582215000 | 1.857678000 | 2.893679000 |
| 6 | 3.951223000 | 0.867437000 | 1.926042000 |
| 1 | 4.277370000 | 1.168753000 | 0.929425000 |
| 6 | 2.780062000 | 0.072792000 | 2.061241000 |
| 6 | 2.010282000 | -0.360618000 | 0.929982000 |
| 6 | 2.411954000 | 0.098715000 | -0.437161000 |
| 6 | 1.687911000 | 1.078758000 | -1.120784000 |
| 6 | 2.046304000 | 1.410082000 | -2.456263000 |
| 1 | 1.451084000 | 2.143515000 | -3.003005000 |
| 6 | 3.122842000 | 0.827060000 | -3.073510000 |
| 1 | 3.378588000 | 1.095567000 | -4.101893000 |
| 6 | 3.923205000 | -0.119017000 | -2.389992000 |
| 6 | 5.059827000 | -0.709361000 | -3.000189000 |
| 1 | 5.314013000 | -0.418059000 | -4.022812000 |
| 6 | 5.830157000 | -1.623426000 | -2.321599000 |
| 1 | 6.707415000 | -2.066975000 | -2.798752000 |
| 6 | 5.485930000 | -1.988343000 | -1.000815000 |
| 1 | 6.101197000 | -2.712402000 | -0.460955000 |
| 6 | 4.382369000 | -1.440819000 | -0.388245000 |
| 1 | 4.127071000 | -1.734058000 | 0.631152000 |
| 6 | 3.566785000 | -0.486966000 | -1.056630000 |
| 6 | -1.097663000 | -3.186173000 | 0.420543000 |
| 6 | -0.436445000 | -4.360764000 | 0.807950000 |
| 1 | 0.651715000 | -4.426655000 | 0.752054000 |
| 6 | -1.159854000 | -5.453208000 | 1.275383000 |
| 1 | -0.634334000 | -6.362837000 | 1.576613000 |
| 6 | -2.551850000 | -5.385779000 | 1.364488000 |
| 1 | -3.117446000 | -6.243002000 | 1.738264000 |

| | | | |
|---|---|---|---|
| 6 | -3.215147000 | -4.222592000 | 0.986675000 |
| 1 | -4.301890000 | -4.154197000 | 1.070932000 |
| 6 | -2.491460000 | -3.127939000 | 0.515056000 |
| 1 | -3.009078000 | -2.209229000 | 0.236991000 |
| 6 | 0.770777000 | -2.381883000 | -1.606908000 |
| 6 | 0.342889000 | -2.084333000 | -2.906717000 |
| 1 | -0.514198000 | -1.420421000 | -3.048353000 |
| 6 | 0.995574000 | -2.627917000 | -4.012194000 |
| 1 | 0.648835000 | -2.387702000 | -5.020304000 |
| 6 | 2.088968000 | -3.471622000 | -3.829183000 |
| 1 | 2.604546000 | -3.897308000 | -4.693614000 |
| 6 | 2.529387000 | -3.766493000 | -2.538718000 |
| 1 | 3.395906000 | -4.415026000 | -2.389940000 |
| 6 | 1.875242000 | -3.226225000 | -1.434935000 |
| 1 | 2.243708000 | -3.449017000 | -0.431460000 |
| 6 | -0.157233000 | 3.338999000 | -1.399817000 |
| 6 | -1.473672000 | 3.567965000 | -1.817951000 |
| 1 | -2.239209000 | 2.817534000 | -1.600261000 |
| 6 | -1.812369000 | 4.741471000 | -2.492917000 |
| 1 | -2.846081000 | 4.906621000 | -2.806313000 |
| 6 | -0.835610000 | 5.696059000 | -2.762927000 |
| 1 | -1.097343000 | 6.615310000 | -3.292876000 |
| 6 | 0.480776000 | 5.477236000 | -2.351960000 |
| 1 | 1.250478000 | 6.224837000 | -2.559367000 |
| 6 | 0.817767000 | 4.310729000 | -1.671334000 |
| 1 | 1.852305000 | 4.156683000 | -1.356794000 |
| 6 | 0.543679000 | 2.464138000 | 1.236020000 |
| 6 | -0.376483000 | 2.224395000 | 2.262456000 |
| 1 | -1.257134000 | 1.604646000 | 2.091685000 |
| 6 | -0.166916000 | 2.762357000 | 3.532359000 |
| 1 | -0.899743000 | 2.554290000 | 4.315151000 |
| 6 | 0.960968000 | 3.538524000 | 3.783962000 |
| 1 | 1.128445000 | 3.958620000 | 4.779061000 |
| 6 | 1.886192000 | 3.774545000 | 2.764443000 |
| 1 | 2.779969000 | 4.371199000 | 2.962628000 |
| 6 | 1.680655000 | 3.241557000 | 1.495883000 |
| 1 | 2.421656000 | 3.418511000 | 0.712877000 |
| 5 | -3.249593000 | -0.259852000 | 2.683542000 |

**Bands decomposition**
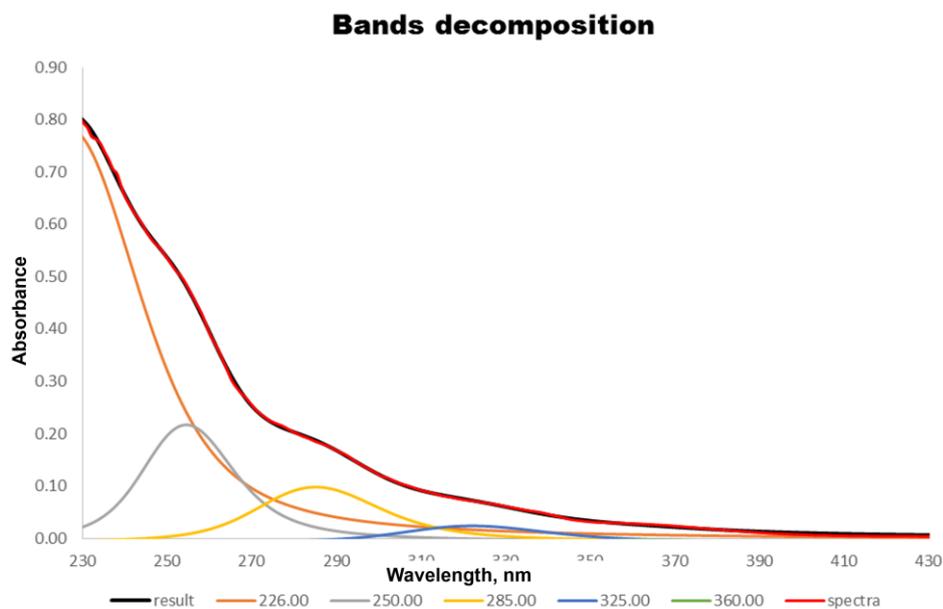


**Figure S1** Bands decomposition for the UV–VIS spectrum of $[Cu(PzH)(BINAP)]BF_4$ in $CH_2Cl_2$ ($c = 3 \cdot 10^{-5}$ mol dm$^{-3}$, $d = 0.1$ cm).
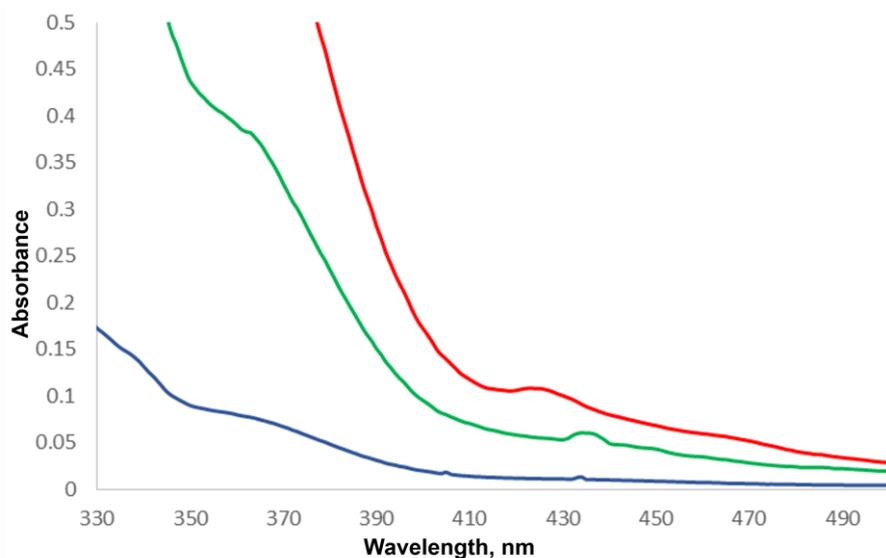


**Figure S2** Absorption spectrum of $[Cu(PzH)(BINAP)]BF_4$ in $CH_2Cl_2$ ($c = 1 \cdot 10^{-4}$ mol dm$^{-3}$) in 1 cm (red), 0.5 cm (green), and 0.1 cm (blue).

## References

S1. *APEX II software package*, Bruker AXS Inc., Madison, WI 5317, 2005.

S2. G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64**, 112.

S3. O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339.

S4. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li,

H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, *Revision D.01*, Gaussian, Inc., Wallingford, CT, 2009.

S5. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158.

S6. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.