**Supporting Information for**

**Elucidation of the Relationship Between Solid-State Photoluminescence and Crystal Structures in 2,6-Substituted Naphthalene Derivatives**

Minoru Yamaji,a,\* Isao Yoshikawa,b Toshiki Mutai,c Hirohiko Houjou,b,d Kenta Goto,e Fumito Tani,e Kengo Suzukif and Hideki Okamotog

a Department of Applied Chemistry, Division of Materials and Environment, Graduate School of Science and Engineering, Gunma University, Ota, Gunma 373-0057, Japan

b Department of Materials and Environmental Science, Institute of Industrial Science, The University of Tokyo, Meguro, Tokyo 153-8505, Japan

c Technology Transfer Service Corporation, Minato, Tokyo 107-6033, Japan

d Environmental Science Center, The University of Tokyo, Bunkyo, Tokyo 113-0033, Japan

e Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 819-0395, Japan.

f Hamamatsu Photonics K.K., Joko-cho, Hamamatsu, Shizuoka 431-3196, Japan

g Department of Chemistry, Faculty of Environment, Life, Natural Sciences and Technology, Okayama University, Okayama 700-8530, Japan

**Contents**

**P. 2 1. Materials, synthetic procedures and analytical data.**

**P. 4 2. 1H and 13C NMR spectra of the synthesized naphthalene derivatives. (Figures S1-3)**

**P. 7 3. X-ray crystallographic analysis data of PhPyNp and DPyNp. (Table S1)**

**P. 8 4. Decay profiles of fluorescence of the DArNps in cyclohexane, acetonitrile and the solid**

**state. (Figures S4-6)**

**P. 9 5. Results of DFT and TD-DFT calculations of the DArNps; atom coordinates and sum of**

**electronic and zero-point energies in chloroform. (Tables S2-4)**

**P. 13 6. HOMO and LUMO surfaces of DArNps in the single crystal. (Figure S7)**

**P. 13 References**

**1. Materials, synthetic procedures and analytical data**

**1-1. Chemicals**

Chloroform, acetonitrile and ethanol (spectroscopic grade from Wako) were used as solvents for the spectral measurements as supplied. The studied PhPyNp and DPyNp were prepared by the procedures described bellows whereas synthetic procedures were described in a previous paper.[1]

**1-2-1. Synthesis of BrPyNp.**

****

To a mixture of dimethoxyethane (10 ml) and H2O (2 ml), dibromonaphthalene (1.0 mmol), 4-pyridyne boronic acid pinacol ester (2.4 mmol) and K2CO3 (690 mg, 5.0 mmol) were added, and the solution was bubbled with pure Ar for 10 min. After tetra(triphenylphosphinate)palladium (0) (120 mg, 10 % mol) was added, the solution was heated at 85 ℃ for 17 h. After cooling to room temperature, benzene (100 ml) was added. The solution was washed twice with brine (100 ml). Then, the organic layer was separated, and dried with Na2SO4. After the organic solvent was evaporated, the crude product was separated by silica gel chromatography with ethyl acetate as the eluent, and purified by recrystallization from ethyl acetate. Yield 52 %.

**1-2-2. Synthesis of PhPyNp.**



To a mixture of dimethoxyethane (10 ml) and H2O (2 ml), BrPyNp (1.0 mmol), phenyl boronic acid (2.4 mmol) and K2CO3 (690 mg, 5.0 mmol) were added, and the solution was bubbled with pure Ar for 10 min. After tetra(triphenylphosphinate)palladium (0) (120 mg, 10 % mol) was added, the solution was heated at 85 ℃ for 3 h. After cooling to room temperature, benzene (100 ml) was added. The solution was washed twice with brine (100 ml). Then, the organic layer was separated, and dried with Na2SO4. After the organic solvent was evaporated, the crude product was separated by silica gel chromatography with ethyl acetate as the eluent, and purified by recrystallization from ethyl acetate. Yield 80 %.

**1-3. Analytical data.**

**2-bromo-6-pyridylnaphthalene; BrPyNp:** 1H NMR (CDCl3, 600 MHz) δH 8.76–8.68 (m, 2H), 8.10–8.02 (m, 2H), 7.90–7.83 (m, 1H), 7.82–7.73 (m, 2H), 7.64–7.58 (m, 3H).

13C NMR (CDCl3, 151 MHz) δC 150.55, 147.94, 136.01, 134.51, 132.01, 130.30, 130.17, 129.95, 128.18, 126.48, 125.77, 121.90, 121.02.

HRMS (FAB) *m*/*z* calcd. for C15H10Br 284.0075, found 284.0075.

Rf on silica TLC developed with ethyl acetate: 0.42.

**2,6-phenylpyridylnaphthalene**; **PhPyNp**:1H NMR (CDCl3, 600 MHz) δH 8.73–8.71 (m, 2H), 8.15 (brs, 1H), 9.08 (brs, 1 H), 8.02 (t, 2H, *J* = 7.9 Hz), 8.83 (dd, 1H, *J* = 8.3, 1.7 Hz), 7.79 (dd, 1H, *J* = 8.4, 1.7 Hz), 7.77–7.73 (m, 2H), 7.68–7.64 (m, 2H), 7.51 (m, 2H), 7.54–7.49 (m, 2H), 7.43–7.39 (m, 1H).

13C NMR (CDCl3, 151 MHz) δC 150.52, 148.34, 140.90, 139.72, 135.56, 133.86, 132.78, 129.40, 129.13, 129.10, 127.79, 127.57, 126.63, 126.34, 125.71, 125.13, 121.94.

HRMS (FAB) *m*/*z* calcd. for C21H15N 281.1204, found 281.1204.

Rf on silica TLC developed with ethyl acetate: 0.22.

**2,6-Dipyridylnaphthalene**; **DPyNp**: 1H NMR (600 MHz, CDCl3) δH 8.72 (m, 4H), 8.17 (m, 2H), 8.05 (d, 2H, *J* = 8.4 Hz), 7.82 (dd, 2H, *J* = 8.4, 1.4 Hz), 7.66 (m, 4H).

13C NMR (151 MHz, CDCl3) δC 150.54, 148.11, 136.53, 133.63, 129.67, 126.39, 125.60, 121.98. The obtained data was identical with those reported previously [2].

**2. 1H and 13C NMR spectra of the synthesized naphthalene derivatives.**



グラフ

自動的に生成された説明

テキスト が含まれている画像

自動的に生成された説明

**Fig. S1** 1H (600 MHz, CDCl3, upper) and 13C (151 MHz, CDCl3, lower) NMR spectra of **BrPyNp**.

****

グラフィカル ユーザー インターフェイス, グラフ

中程度の精度で自動的に生成された説明

ダイアグラム が含まれている画像

自動的に生成された説明

**Fig. S2** 1H (600 MHz, CDCl3, upper) and 13C (151 MHz, CDCl3, lower) NMR spectrum of **PhPyNp**.



グラフ

自動的に生成された説明

グラフ, ヒストグラム

自動的に生成された説明

**Fig. S3** 1H (600 MHz, CDCl3, upper) and 13C (151 MHz, CDCl3, lower) NMR spectra of **DPyNp**.

**3. X-ray crystallographic analysis data of PhPyNp and DPyNp**

Crystallographic data of the studied PhPyNp and DPyNp are listed in Table S1. The structures were solved by direct methods (shelxs-2013)[3] and refined on *F*2 by full-matrix least-squares techniques (shelxl-2018)[4] using the Yadokari- XG software package.[5] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were refined isotropically, whereby hydrogen positions are based on stereochemical considerations.

**Table S1** Crystallographic data of compounds **PhPyNp** and **DPyNp**

|  |  |  |
| --- | --- | --- |
| Compound | **PhPyNp**  CCDC 2452168 | **DPyNp**  CCDC 2452169 |
| Empirical formula (FW) | C21H15N (281.34) | C20H14N2 (282.33) |
| Crystal dimensions | 0.20 x 0.20 x 0.01 mm3 | 0.25 x 0.15 x 0.03 mm3 |
| Crystal system | orthorhombic | orthorhombic |
| *a* | 5.9699(5) Å | 6.9315(1) Å |
| *b* | 7.4311(5) Å | 10.5681(3) Å |
| *c* | 31.359(2) Å | 18.6878(5) Å |
| *a* | 90 ° | 90 ° |
| *b* | 90 ° | 90 ° |
| *g* | 90° | 90 ° |
| *V* | 1391.19(18) Å3 | 1368.93(6) Å3 |
| Space group | *P*212121 | *P*bca |
| *Z* | 4 | 4 |
| *Z*’ | 1 | 0.5 |
| *ρ*calcd | 1.343 g/cm3 | 1.370 g/cm3 |
| *F*(000) | 592.0 | 592.0 |
| *m*(CuKa) | 0.595 mm−1 | 0.629 mm−1 |
| 2*θ*max | 145.488 ° | 145.762 ° |
| Obs. Temp. | 100 K | 93 K |
| Total reflections measured | Total: 12610  Unique: 2700  (Rint = 0.1001) | Total: 7307  Unique: 1353  (Rint = 0.0254) |
| Number of parameters | 200 | 100 |
| Data/parameter ratio | 13.5 | 13.5 |
| *R1* (I>2.00s(I)) | 0.1410 (2199) | 0.0390 (1258) |
| *wR*2  (All reflections) | 0.3813(2700) | 0.1062 (1353) |
| GOF | 1.627 | 1.078 |
| Max/min residual density | 0.984 / -0.460 e- Å3 | 0.191 / -0.290 e- Å3 |

**4. Decay profiles of fluorescence of the DArNps in chroroform, acetonitrile and the solid state.**

Fig. S4 shows decay profiles of fluorescence for DArNps in chloroform.

  

**Fig. S4** Decay profiles of fluorescence for DArNps in chloroform at 295 K. Ex and Mon in the figures indicate the excitation and monitoring wavelengths, respectively.

Fig. S5 shows decay profiles of PhPyNp and DPyNp in acetonitrile.

 

**Fig. S5** Decay profiles of fluorescence for PhPyNp and DPyNp in acetonitrile at 295 K. Ex and Mon in the figures indicate the excitation and monitoring wavelengths, respectively.

Fig. S6 shows decay profiles for PhPyNp and DPyNp in the solid state.

　　　

**Fig. S6** Decay profiles of fluorescence for PhPyNp and DPyNp in the solid state at 295 K. Ex and Mon in the figures indicate the excitation and monitoring wavelengths, respectively.

**5. Results of DFT and TD-DFT calculations of the DPNs; atom coordinates and sum of electronic and zero-point energies in chloroform.**

The calculation was carried out at the DFT level, using the Gaussian 09 software package [6]. The geometries of DPNswere fully optimized by using the 6-31+G(d,p) base set at the B3LYP method.Atom coordinates for the optimized geometries of DArNps in chloroform are as follows.

**Table S2** Atom coordinates for the optimized geometry of DPhNp.

|  |  |  |  |
| --- | --- | --- | --- |
| Atom | X | Y | Z |
| C | 4.858915 | -1.122514 | 0.400258 |
| C | 6.244873 | -0.959027 | 0.454184 |
| C | 6.827371 | 0.252454 | 0.068945 |
| C | 6.009724 | 1.297957 | -0.371772 |
| C | 4.624130 | 1.133430 | -0.426391 |
| C | -4.858902 | 1.122637 | -0.399977 |
| C | -6.244884 | 0.959194 | -0.453864 |
| C | -6.827373 | -0.252370 | -0.068919 |
| C | -6.009724 | -1.298029 | 0.371430 |
| C | -4.624134 | -1.133543 | 0.426033 |
| C | 4.022926 | -0.078654 | -0.038467 |
| C | -4.022936 | 0.078646 | 0.038446 |
| C | -0.616363 | 1.682694 | 0.540821 |
| C | -1.979727 | 1.501361 | 0.486531 |
| C | -2.547165 | 0.252345 | 0.089350 |
| C | -1.687844 | -0.783840 | -0.245933 |
| C | 0.616362 | -1.682727 | -0.540760 |
| C | 1.979728 | -1.501426 | -0.486419 |
| C | 2.547187 | -0.252395 | -0.089336 |
| C | 0.277645 | 0.629557 | 0.198463 |
| C | -0.277648 | -0.629567 | -0.198501 |
| C | 1.687840 | 0.783823 | 0.245859 |
| H | 4.420885 | -2.062367 | 0.722956 |
| H | 6.868554 | -1.776607 | 0.804384 |
| H | 7.905168 | 0.379547 | 0.109272 |
| H | 6.451052 | 2.240231 | -0.683955 |
| H | 4.004437 | 1.945335 | -0.795164 |
| H | -4.420912 | 2.062568 | -0.722485 |
| H | -6.868520 | 1.776935 | -0.803760 |
| H | -7.905173 | -0.379466 | -0.109160 |
| H | -6.451045 | -2.240421 | 0.683269 |
| H | -4.004437 | -1.945594 | 0.794484 |
| H | -0.207061 | 2.638828 | 0.856583 |
| H | -2.638418 | 2.315482 | 0.772858 |
| H | -2.090358 | -1.737873 | -0.575543 |
| H | 0.207031 | -2.638867 | -0.856482 |
| H | 2.638409 | -2.315620 | -0.772585 |
| H | 2.090371 | 1.737856 | 0.575439 |

Sum of electronic and zero-point energies = -847.927230874 Hartree

**Table S3** Atom coordinates for the optimized geometry of PhPyNp.

|  |  |  |  |
| --- | --- | --- | --- |
| Atom | X | Y | Z |
| C | -1.982159 | 1.581541 | 0.019808 |
| C | -2.546838 | 0.270657 | -0.002265 |
| C | -1.691655 | -0.821184 | -0.017386 |
| C | -0.281799 | -0.660582 | -0.012025 |
| C | 0.273412 | 0.659526 | 0.002670 |
| C | -0.618829 | 1.768416 | 0.019527 |
| C | 0.610161 | -1.769552 | -0.017169 |
| C | 1.973451 | -1.581365 | -0.013767 |
| C | 2.540626 | -0.271007 | -0.004677 |
| C | 1.683511 | 0.819581 | 0.006004 |
| C | 4.016110 | -0.089204 | -0.002851 |
| C | -4.019649 | 0.088170 | -0.002284 |
| C | -4.869176 | 0.936268 | 0.727849 |
| C | -6.246699 | 0.719187 | 0.700574 |
| N | -6.835596 | -0.267745 | 0.006630 |
| C | -6.023865 | -1.076872 | -0.693317 |
| C | -4.636744 | -0.942206 | -0.731634 |
| C | 4.851091 | -0.955823 | 0.726362 |
| C | 6.236465 | -0.779350 | 0.733182 |
| C | 6.817723 | 0.266168 | 0.008822 |
| C | 6.000265 | 1.132866 | -0.723455 |
| C | 4.615222 | 0.955529 | -0.730750 |
| H | -2.640588 | 2.444391 | 0.009564 |
| H | -2.095222 | -1.829901 | -0.008277 |
| H | -0.207714 | 2.774407 | 0.022397 |
| H | 0.198952 | -2.775366 | -0.036378 |
| H | 2.632705 | -2.443536 | -0.041085 |
| H | 2.087690 | 1.827676 | 0.037980 |
| H | -4.468219 | 1.743870 | 1.331590 |
| H | -6.909060 | 1.367992 | 1.269357 |
| H | -6.507837 | -1.869577 | -1.259488 |
| H | -4.049886 | -1.619803 | -1.343005 |
| H | 4.413205 | -1.760664 | 1.309628 |
| H | 6.861064 | -1.454700 | 1.310921 |
| H | 7.895228 | 0.402076 | 0.012737 |
| H | 6.441382 | 1.941683 | -1.299001 |
| H | 3.993737 | 1.621084 | -1.322664 |

Sum of electronic and zero-point energies = -863.962821773 Hartree

**Table S4** Atom coordinates for the optimized geometry of DPyNp.

|  |  |  |  |
| --- | --- | --- | --- |
| Atom | X | Y | Z |
| C | -1.976850 | -1.572780 | 0.005109 |
| C | -2.565174 | -0.263363 | 0.000551 |
| C | -1.688113 | 0.817857 | -0.003531 |
| C | -0.277721 | 0.653575 | -0.003246 |
| C | 0.277634 | -0.653728 | 0.001774 |
| C | -0.615948 | -1.761156 | 0.005922 |
| C | 0.615915 | 1.760959 | -0.007752 |
| C | 1.976813 | 1.572579 | -0.006870 |
| C | 2.565127 | 0.263156 | -0.001475 |
| C | 1.688045 | -0.818031 | 0.002626 |
| C | 4.059573 | 0.078787 | -0.000362 |
| C | -4.059577 | -0.078934 | 0.000507 |
| C | 4.958285 | 1.164238 | -0.002897 |
| C | 6.334602 | 0.942698 | -0.001769 |
| N | 6.896905 | -0.273388 | 0.001765 |
| C | 6.053626 | -1.315897 | 0.004239 |
| C | 4.666198 | -1.193984 | 0.003305 |
| C | -4.958442 | -1.164124 | -0.013215 |
| C | -6.334742 | -0.942318 | -0.012965 |
| N | -6.896824 | 0.273786 | 0.000219 |
| C | -6.053355 | 1.316105 | 0.013541 |
| C | -4.665979 | 1.193896 | 0.014133 |
| H | -2.614310 | -2.445691 | 0.008758 |
| H | -2.060950 | 1.833468 | -0.007553 |
| H | -0.201521 | -2.765827 | 0.009939 |
| H | 0.201505 | 2.765642 | -0.011915 |
| H | 2.614265 | 2.445495 | -0.010341 |
| H | 2.060796 | -1.833659 | 0.006695 |
| H | 4.602598 | 2.185139 | -0.005680 |
| H | 7.031537 | 1.776409 | -0.003748 |
| H | 6.525345 | -2.294807 | 0.007069 |
| H | 4.069820 | -2.096062 | 0.005462 |
| H | -4.602984 | -2.185049 | -0.024752 |
| H | -7.031836 | -1.775816 | -0.024080 |
| H | -6.524958 | 2.295004 | 0.024625 |
| H | -4.069374 | 2.095762 | 0.025889 |

Sum of electronic and zero-point energies = -847.880413607 Hartree

**6. HOMO and LUMO surfaces calculated for single crystal structures.**



**Fig. S7** HOMO and LUMO surfaces of DArNps in the single crystal.

**References**

[1] M. Yamaji, T. Mutai, I. Yoshikawa, H. Houjou, H. Okamoto, *Molecules* **2024**, *29*, 5941.

[2] D. Li, W. Hu, J. Wang, Q. Zhang, X. M. Cao, X. Ma, H. Tian, *Chem. Sci.* **2018**, *9*, 5709-5715.

[3] G. M. Sheldrick, *Acta Cryst. A* **2008**, *72*, 112-122.

[4] G. Sheldrick, *Acta Crystallogr. C* **2015**, *71*, 3-8.

[5] C. Kabuto, S. Akine, T. Nemoto, E. Kwon, *J. Cryst. Soc. Jpn.* **2009**, *51*, 218-224.

[6] 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. J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision D.01*,Gaussian, Inc., Wallingford CT, **2010**.