Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supplementary Information

Development of Aryl-substituted 2-phenylimidazo[1,2-*a*]pyridines (PIP) with Various Colors of Excited-State Intramolecular Proton Transfer (ESIPT) Luminescence in the Solid State

Toshiki Mutai,* Tatsuya Ohkawa, Hideaki Shono and Koji Araki*

Department of Materials and Environmental Science, Institute of Industrial Science, the University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan

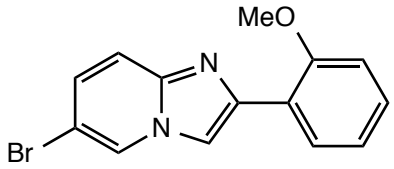
E-mail: mutai@iis.u-tokyo.ac.jp, *araki@iis.u-tokyo.ac.jp*

Synthesis

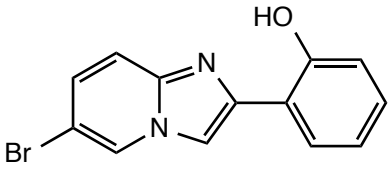
2-(2'-Hydroxyphenyl)-6-(bromo)imidazo[1,2-*a*]pyridine (**11**)

An acetonitrile (50 mL) solution of 2-bromo-1-(2-methoxyphenyl)ethanone (2.91 g, 12.7 mmol), 2-amino-5-bromopyridine (2.20 g, 12.7 mmol) and $NaHCO_3$ (2.15 g, 25.6 mmol) was refluxed for 4 h. After cooling, insoluble solid was filtered off. Evaporation of the filtrate afforded crude product, which was then purified by a silica gel column chromatography (chloroform–ethyl acetate = 5:1) to give 2-(2'-methoxyphenyl)-6-bromoimidazo[1,2-*a*] pyridine (**11Me**) as white powder (2.77 g, 72 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 4.05 (s, 3H), 7.04 (d, *J* = 8.4 Hz, 1H), 7.21 (t, *J* = 14.4 Hz, 1H), 7.48 (t, *J* = 14.4 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 8.26 (s, 1H), 8.40 (d, *J* = 6.0 Hz, 1H), 8.54 (s, 1H), 8.63 (d, *J* = 9.6 Hz, 1H).

Then to a cooled anhydrous dichloromethane solution (5 mL, -78 °C) of well-dried **11Me** (0.23 g, 0.76 mmol) was dropwise added a dichloromethane solution of boron tribromide (1.0 M, 4 mL). The reaction mixture was allowed to reach room temperature and further stirred overnight. A saturated aqueous $NaHCO_3$ was slowly added with stirring, and then separated with water and chloroform. After washing the organic layer with saturated aqueous $NaHCO_3$ and water, and drying over $MgSO_4$, the organic layer was evaporated to yield **11** as crude product. Reprecipitation from chloroform gave white powder (0.17 g, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 6.89 (t, *J* = 14.0 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 7.22 - 7.31 (m, 2H), 7.50 (d, *J* = 9.6 Hz, 1H), 7.57 (d, *J* = 6.0 Hz, 1H), 7.84 (s, 1H), 8.30 (s, 1H).



11Me

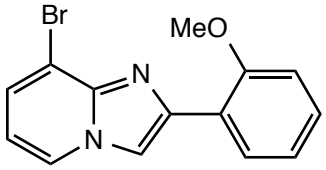


11

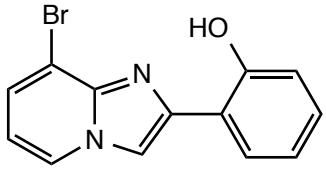
2-(2'-Hydroxyphenyl)-8-(bromo)imidazo[1,2-*a*]pyridine (**12**)

At first, 2-(2'-methoxyphenyl)-8-bromoimidazo[1,2-*a*]pyridine (**12Me**) was prepared by the similar condition as **11Me** using 2-amino-3-bromopyridine instead of 2-amino-5-bromopyridine. Purified by a silica gel column chromatography (chloroform–ethyl acetate = 10:1). Yield 72 %. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.00 (s, 3H), 6.63 (t, *J* = 14.4 Hz, 1H), 6.99 (s, *J* = 8.4 Hz, 1H), 7.11 (t, *J* = 14.0 Hz, 1H), 7.32 (t, *J* = 14.0 Hz, 1H), 7.41 (d, *J* = 6.4 Hz, 1H), 8.10 (d, *J* = 6.0 Hz, 1H), 8.23 (s, 1H), 8.51 (d, *J* = 6.0 Hz, 1H).

Then **12Me** was demethylated by the same condition as **11Me**. The crude product (**12**) was purified by a silica gel chromatography ($CHCl_3$) to give white powder (72 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.75 (t, *J* = 14.0 Hz, 1H), 6.89 (t, *J* = 13.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 13.6 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.57 (d, *J* = 6.4 Hz, 1H), 7.93 (s, 1H), 8.13 (d, *J* = 6.0 Hz, 1H).



12Me

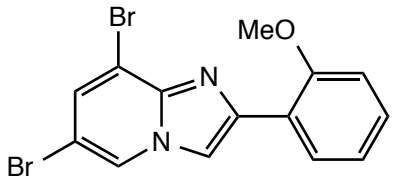


12

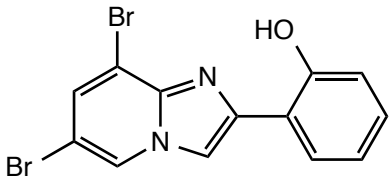
2-(2'-Hydroxyphenyl)-6,8-dibromoimidazo[1,2-*a*]pyridine (**13**)

At first, 2-(2'-methoxyphenyl)-6,8-dibromoimidazo[1,2-*a*]pyridine (**13Me**) was prepared by the similar condition as **11Me** using 2-amino-3,5-dibromopyridine instead of 2-amino-5-bromopyridine, and refluxed for 3 days. Purified by a flash column chromatography on a silica gel (eluent: $CHCl_3$ / hexane = 7 : 2) gave pale-yellow powder (1.67 g, 48.1 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.48 (1H, dd, *J* = 7.8, 1.7 Hz), 8.23 (1H, d, *J* = 1.7 Hz), 8.22 (1H, s), 7.50 (1H, d, *J* = 1.5 Hz), 7.33 (1H, ddd, *J* = 8.7, 7.0, 1.3 Hz), 7.10 (1H, td, *J* = 7.5, 0.8 Hz), 6.99 (1H, d, *J* = 8.3 Hz), 3.98 (3H, s). MS (FAB): m/z: 380.3 (calcd. for $C_{14}H_{11}Br_2N_2O$ $[M + H]^+$ = 380.92)

Then **13Me** was demethylated by the same condition as **11Me**. The crude product (**13**) was recrystallized from ethanol to give colourless microcrystal (572 mg, 77.7 %).
^{1}H NMR (400 MHz, DMSO-D_6) δ = 11.16 (1H, s), 9.02 (1H, t, *J* = 1.5 Hz), 8.57 (1H, d, *J* = 1.2 Hz), 8.04 (1H, dt, *J* = 7.8, 1.5 Hz), 7.86 (1H, t, *J* = 1.6 Hz), 7.23-7.21 (1H, m), 6.98-6.92 (2H, m). MS (FAB): m/z: 366.9 (calcd. for $C_{13}H_9Br_2N_2O$ $[M + H]^+$ = 366.91)



13Me

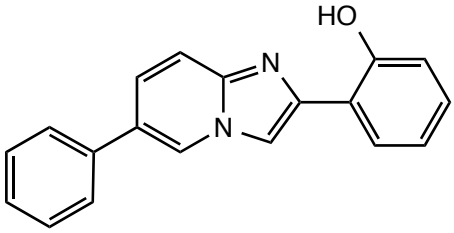


13

General synthetic procedure for 6- and 8-aryl HPIPs (2–7)

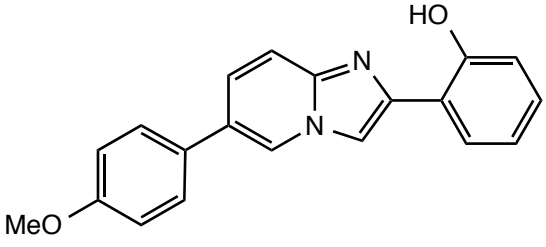
A dioxane–water (3:1) solution (30 mL) of **11** (for **2**–**4**) or **12** (for **5**–**7**) (0.20 g, 0.70 mmol), corresponding arylboronic acid (1.2 equiv.), potassium carbonate (0.385 g, 2.79 mmol), and tetrakis(triphenylphosphine)palladium(0) (0.041 g, 0.035 mmol) was refluxed for 8–27 h. After addition of saturated aqueous NH_4Cl, the reaction mixture was extracted with chloroform. The organic layer was washed with water and brine, then dried over $MgSO_4$. Evaporation afforded crude product, which was further purified by a suitable method.

2-(2'-Hydroxyphenyl)-6-(phenyl)imidazo[1,2-*a*]pyridine (2): Refluxed for 8 h. Crude product was purified by a silica gel column chromatography (chloroform) to give white powder. M. p. 154.4–155.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 6.90 (t, *J* = 14.0 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 4.8 Hz, 1H) 7.42 - 7.68 (m, 8H), 7.92 (s, 1H), 8.33 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 107.06, 116.17, 116.60, 117.73, 119.00, 122.60, 125.73, 125.98, 126.97, 127.74, 128.13, 129.21, 129.73, 136.96, 142.77, 145.81, 157.33. Calcd. for $C_{19}H_{14}N_2O$: C, 79.70; H, 4.93; N, 9.78 %. Found: C, 79.57; H, 4.96; N, 9.66 %.



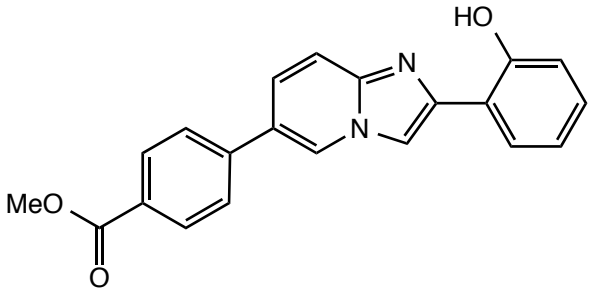
2

2-(2'-Hydroxyphenyl)-6-(*p*-methoxyphenyl)imidazo[1,2-*a*]pyridine (3): Refluxed in dioxane–water (3:1) for 17 h. Crude product was purified by a silica gel column (benzene) to give white solid. Yield 96 %. M. p. 143.5–144.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 3.88 (s, 3H), 6.90 (t, *J* = 15.2 Hz, 1H), 7.01–7.06 (m, 3H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.45–7.51 (m, 3H),7.62 (t, *J* = 16.4 Hz, 2H), 7.90 (s, 1H), 8.27 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 55.42, 106.98, 114.61, 116.22, 116.45, 117.70, 118.96, 121.92, 125.69, 125.96, 127.40, 128.05, 129.33, 129.64, 142.59, 145.63, 157.30, 159.69. HRMS (FAB): m/z: 317.1283 (Calcd. for $C_{20}H_{16}N_2O_2$ [M+H] = 317.1290).



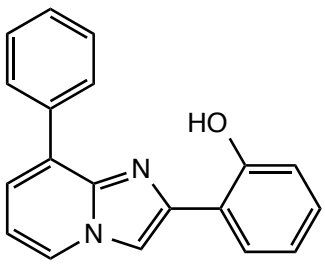
3

2-(2'-Hydroxyphenyl)-6-(*p*-methoxycarbonylphenyl)imidazo[1,2-*a*]pyridine (4): Refluxed in dioxane–water (3:1) for 8 h. Crude product was purified by a silica gel column (benzene) to give a pale pink solid. Yield 31 %. M. p. 202.4–203.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 3.97 (s, 3H), 6.91 (t, *J* = 13.6 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 7.25 - 7.26 (m, 2H), 7.52 (d, *J* = 7.2 Hz, 1H), 7.61 - 7.70 (m, 4H), 7.94 (s, 1H), 8.16 (d, *J* = 4.4 Hz, 1H), 8.40 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 52.32, 107.19, 116.87, 117.79, 119.06, 123.08, 125.47, 125.78, 126.61, 126.84, 129.73, 129.90, 130.50, 141.36, 157.34, 166.65. Calcd. for $C_{21}H_{16}N_2O_3$: C, 73.24; H, 4.68; N, 8.13 %. Found: C, 73.48; H, 4.64; N, 8.08 %.



4

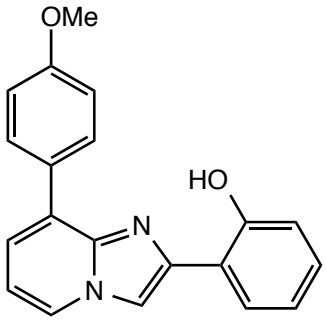
2-(2'-Hydroxyphenyl)-8-phenylimidazo[1,2-*a*]pyridine (5): Refluxed in dioxane for 24 h. Crude product was purified by a silica gel column (chloroform) to give a pale pink solid. Yield 80 %. M. p. 91.4–93.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 6.89 (t, *J* = 15.2 Hz, 1H), 6.94 (t, *J* = 14.0 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 7.24 (t, *J* = 10.0 Hz, 1H), 7.33 (d, *J* = 6.0 Hz, 1H), 7.43 (t, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 13.2 Hz, 2H), 7.60 (d, *J* = 6.0 Hz, 1H), 7.91 (s, 1H), 7.94 (d, *J* = 6.8 Hz, 2H), 8.12 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 107.15, 113.51, 116.08, 117.60, 118.93, 123.61, 124.28, 125.64, 128.56, 128.61, 129.66, 135.92, 142.16, 145.07, 157.22. HRMS (FAB): Calcd. for $C_{19}H_{14}N_2O$ m/z 287.1184, found 287.1175.



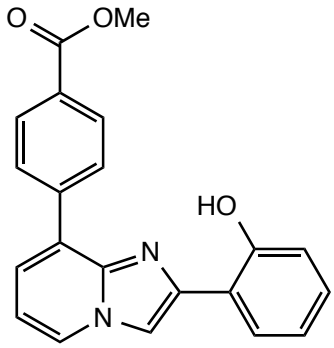
5

2-(2'-Hydroxyphenyl)-8-(*p*-methoxyphenyl)imidazo[1,2-*a*]pyridine (6): Refluxed in dioxane–water (10:1) for 24 h. Crude product was purified by a silica gel column (chloroform) to give a pale pink solid. Yield 66 %. M. p. 49.5-51.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 3.88 (s, 3H), 6.83 - 6.91 (m, 3H), 7.05 (t, *J* = 6.8 Hz, 1H), 7.24 (t, *J* = 11.2 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 7.83 (s, 1H), 7.91 (d, *J* = 7.2 Hz, 3H), 8.00 (d, *J* = 6.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 55.24, 107.10, 113.43, 113.92, 116.11, 117.47, 118.88, 122.69, 123.67, 125.58, 128.19, 128.97, 129.50, 129.64, 142.02, 144.67, 157.12, 159.79. HRMS (FAB): m /z: 317.1295 (calcd. for $C_{20}H_{16}N_2O_2$ [M+H] = 317.1290).

2-(2'-Hydroxyphenyl)-8-(*p*-methoxycarbonylphenyl)imidazo[1,2-*a*]pyridine (7): Refluxed in dioxane for 27 h. Crude product was purified by a silica gel column (chloroform) and recrystallized from ethanol to give a pale pink crystal. Yield 50 %. M. p. 224.9–225.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 3.96 (s, 3H), 6.90 (t, *J* = 14.0 Hz, 1H), 6.99 – 7.03 (m, 2H), 7.24 (d, *J* = 5.2 Hz, 1H), 7.40 (d, *J* = 6.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.97 (s, 1H), 8.03 (d, *J* = 7.2 Hz, 2H), 8.20 (d, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 52.24, 107.32, 113.47, 115.92, 117.70, 119.04, 124.12, 125.01, 125.70, 128.56, 129.87, 129.90, 129.99, 140.44, 141.88, 145.34, 157.23, 166.81. HRMS (FAB): m /z: 345.1241 (calcd. for $C_{21}H_{16}N_2O_3$ [M+H] = 345.1239)



6



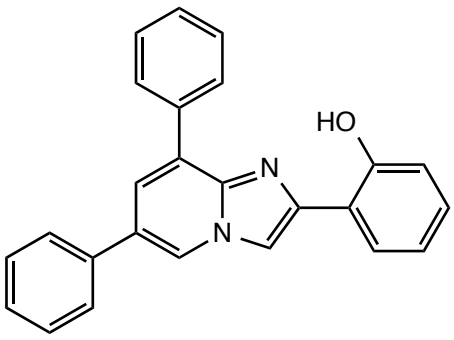
7

2-(2'-Hydroxyphenyl)-6,8-diarylimidazo[1,2-*a*]pyridine (**8** and **9**)

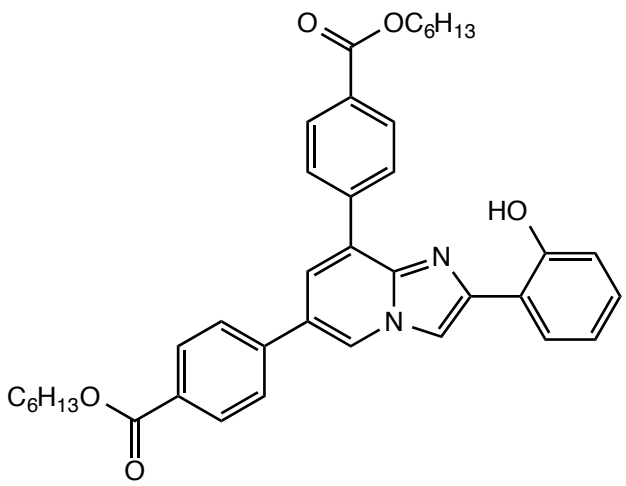
A dioxane-water (3:1, 20 mL) solution of **13** (602 mg, 1.64 mmol), corresponding arylboronic acid (2.2 equiv.), potassium carbonate (910 mg, 6.58 mmol), and tetrakis-(triphenylphosphine)palladium(0) (114 mg, 0.099 mmol) was stirred overnight at 90 °C. After addition of saturated aqueous NH_4Cl, the reaction mixture was extracted with $CHCl_3$. The organic layer was washed with water and saturated aqueous NaCl, dried over Na_2SO_4, and evaporated to afford crude product.

2-(2'-Hydroxyphenyl)-6,8-diphenylimidazo[1,2-*a*]pyridine (8): Purified by flash column chromatography on a silica gel (eluent: hexane / $CHCl_3$ = 3 : 1) and recrystallized from ethanol to give **8** as a pale pink crystal (71 %). M. p. 185.5–186.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 12.83 (1H, s), 8.32 (1H, d, *J* = 1.7 Hz), 8.00 (2H, dt, *J* = 9.5, 4.8 Hz), 7.98 (1H, s), 7.64-7.61 (4H, m), 7.57-7.41 (6H, m), 7.24-7.22 (1H, m), 7.02 (1H, dd, *J* = 8.3, 1.0 Hz), 6.90 (1H, td, *J* = 7.4, 1.1 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.13, 145.42, 141.41, 136.92, 135.79, 129.63, 129.30, 129.10, 128.62, 128.59, 128.55, 128.06, 127.93, 126.90, 125.59, 124.33, 121.43, 118.91, 117.56, 116.04, 107.51. MS (FAB): m/z: 363.3 (calcd $[M + H]^+$ = 363.15). Calcd. for $C_{25}H_{18}N_2O$: C, 82.85; H, 5.01; N, 7.73 %. Found: C, 82.96; H, 5.02; N, 7.41 %.

2-(2'-Hydroxyphenyl)-6,8-di{*p*-(hexyloxycarbonyl)phenyl}imidazo[1,2-*a*]pyridine (9): Purified by flash column chromatography on a silica gel (eluent: hexane / $CHCl_3$ = 1 : 1) and recrystallized from ethanol to give **9** as a pale pink powder (66 %). M. p. 141.7–142.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 12.60 (1H, s), 8.39 (1H, d, *J* = 1.5 Hz), 8.19 (4H, dd, *J* = 13.1, 8.4 Hz), 8.07 (2H, d, *J* = 8.3 Hz), 8.00 (1H, s), 7.69 (2H, d, *J* = 8.3 Hz), 7.62 (2H, dd, *J* = 6.6, 3.3 Hz), 7.24 (1H, dd, *J* = 4.3, 2.1 Hz), 7.02 (1H, d, *J* = 8.3 Hz), 6.91 (1H, t, *J* = 7.4 Hz), 4.36 (4H, td, *J* = 6.7, 2.5 Hz), 1.80 (4H, m), 1.49-1.46 (4H, m), 1.37 (8H, m), 0.93 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.04, 165.97, 156.99, 145.64, 141.01, 140.76, 139.72, 130.42, 130.25, 130.05, 129.83, 129.70, 128.31, 128.13, 126.61, 125.60, 124.02, 122.46, 118.98, 117.56, 115.66, 107.78, 65.37, 65.28, 31.52, 31.49, 28.72, 25.76, 25.74, 22.60, 14.09. MS (FAB): m/z: 619.5 (calcd $[M + H]^+$ = 619.32). Calcd. for $C_{39}H_{42}N_2O_5$: C, 75.70; H, 6.84; N, 4.53 %. Found: C, 75.69; H, 6.85; N, 4.27 %.



8



9

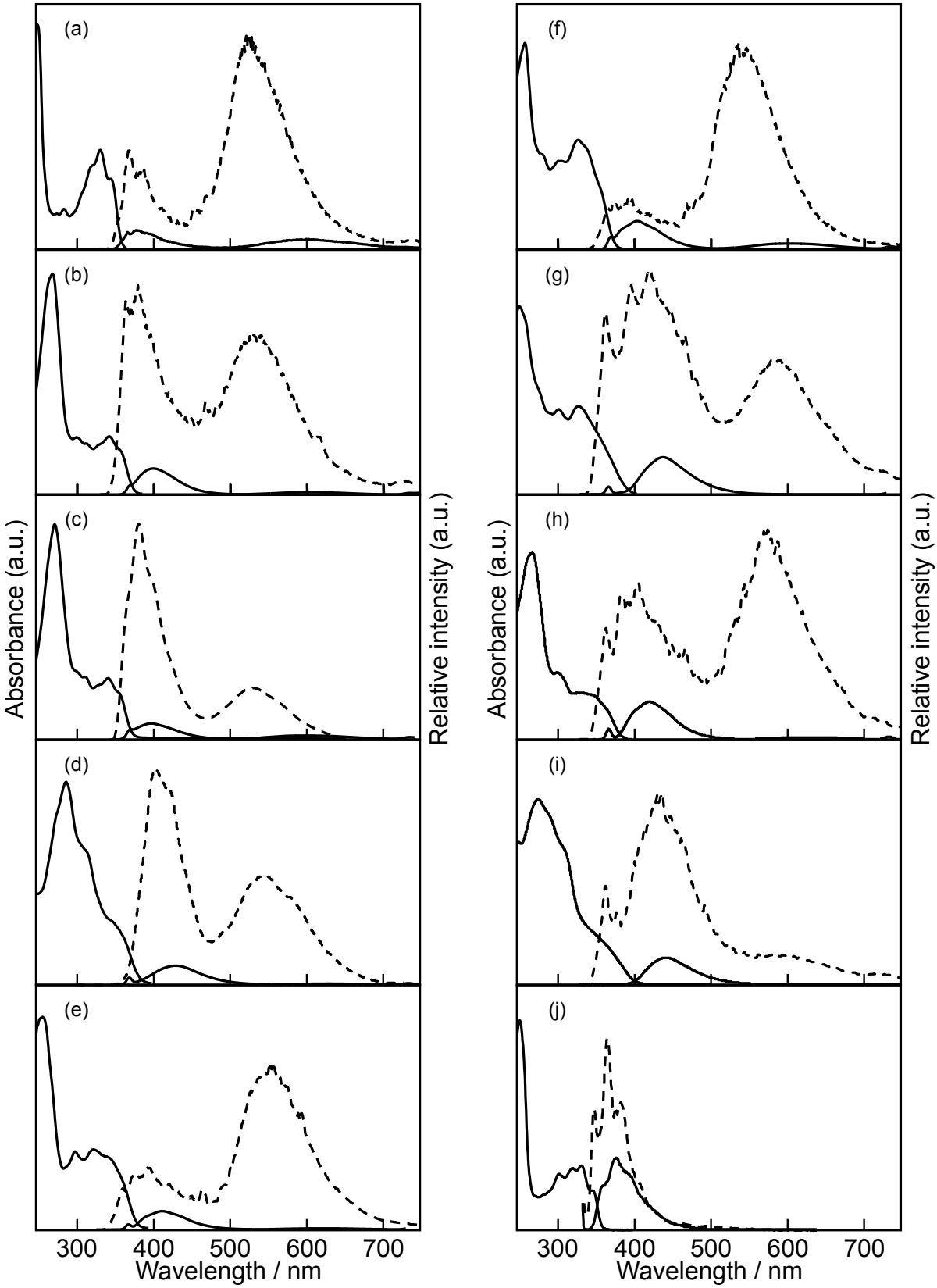


Figure S1. Absorption and luminescence spectra of **1** (a) through **10** (j) in tetrahydrofuran (THF). Absorption and fluorescence in fluid solution (solid line), and fluorescence in frozen solution at 77 K (broken line).

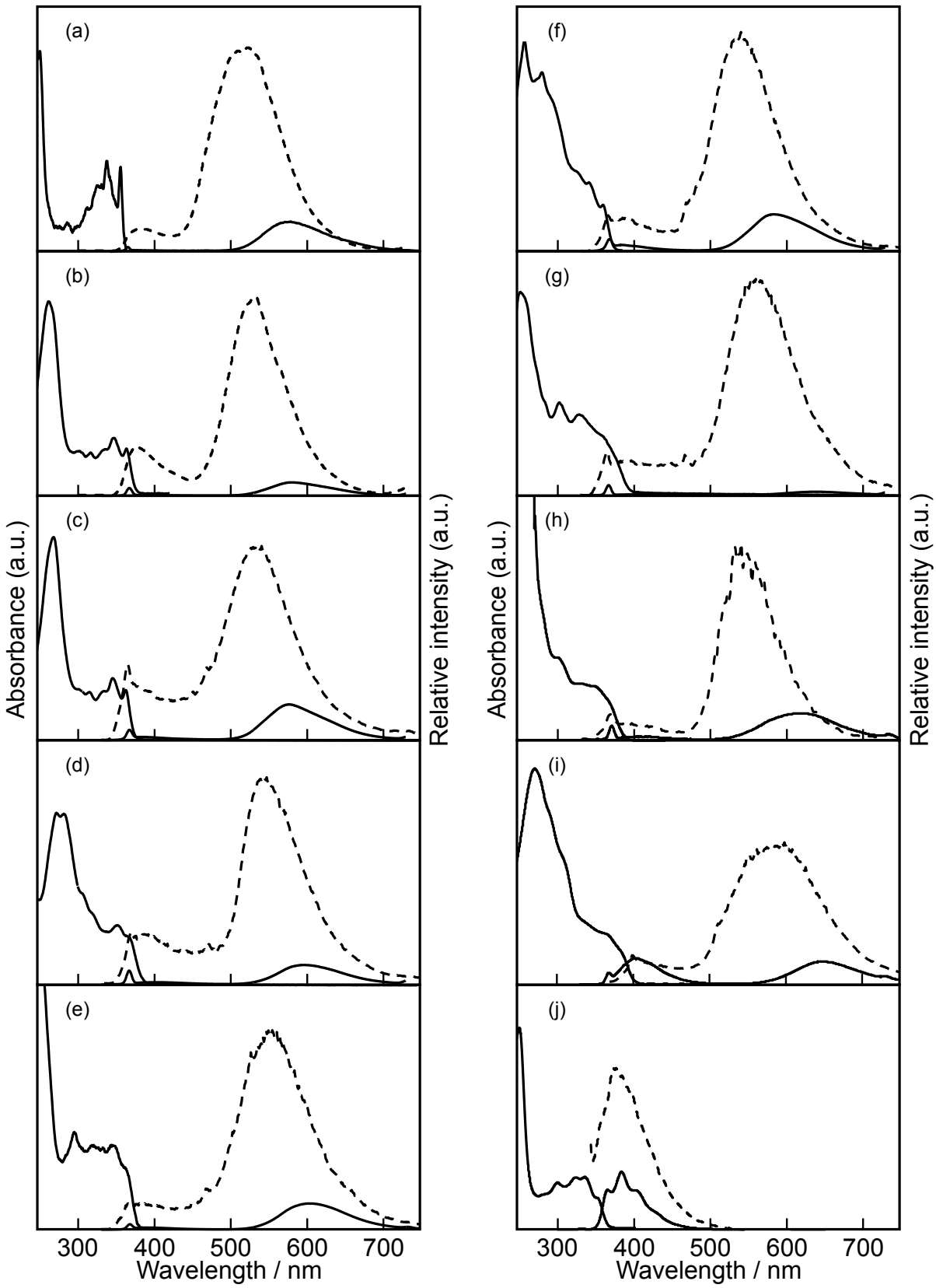


Figure S2. Absorption and luminescence spectra of **1** (a) – **7** (g), **9** (i), **10** (j) in cyclohexane, and **8** (h) in benzene. Absorption and fluorescence in fluid solution (solid line), fluorescence in frozen solution at 77 K (broken line).

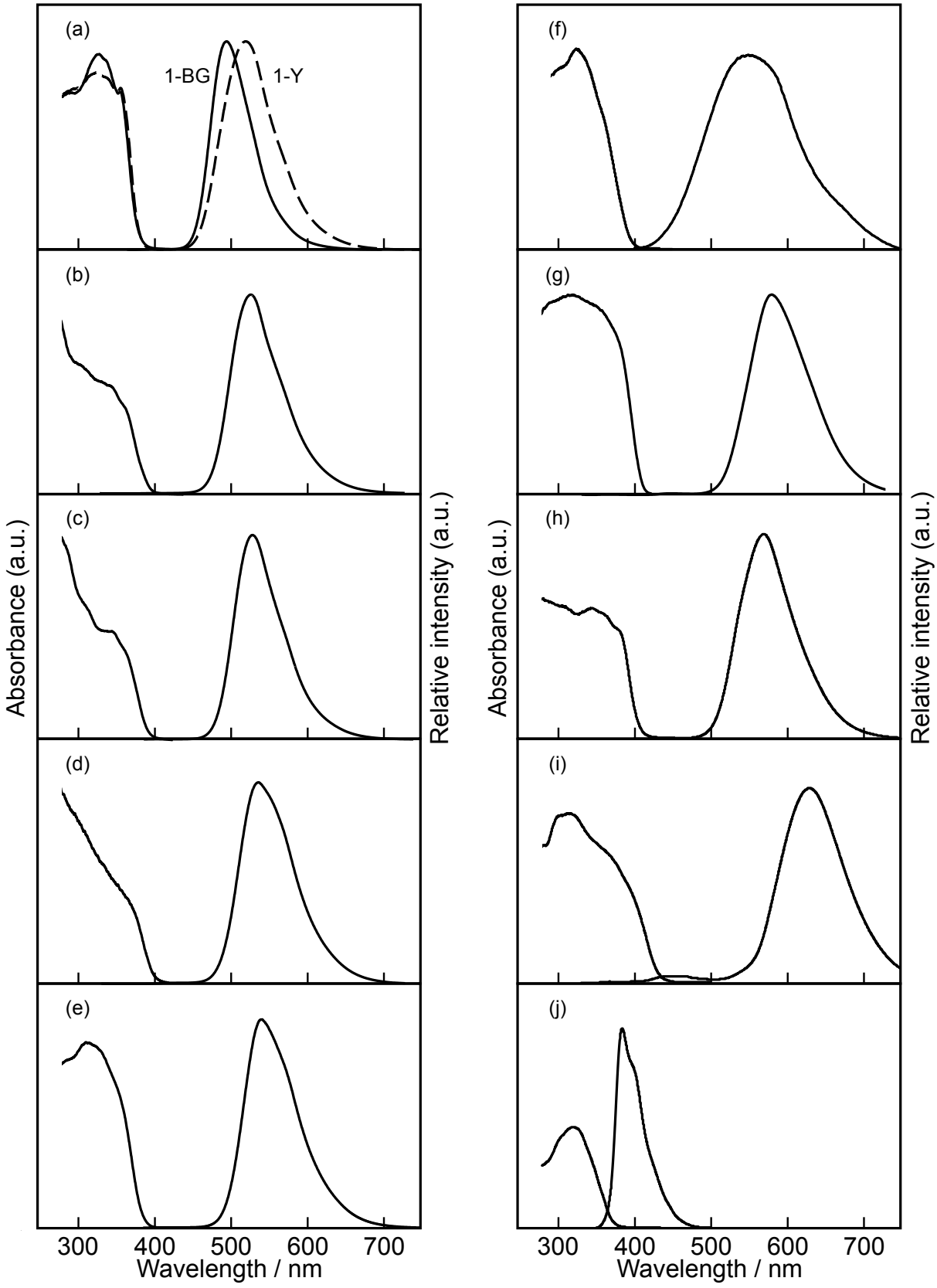


Figure S3. Absorption (Kubelka-Munk) and luminescence spectra of **1** (a) through **10** (j) in the solid state.

X-ray crystallographic data

X-ray diffraction data were collected on a Rigaku VariMax DW with Saturn 724 diffractometer equipped with a graphite-monochromatized Mo *K*α source (crystal **3**) or a MacScience DIP-Labo with graphite-monochromatized Cu *K*α radiation (crystal **4**, **7** and **8**). The structure was solved by direct method SHELXS-2014 and expanded by subsequent Fourier synthesis. The refinement by full matrix least-squares calculations was performed using SHELXL-2014.

Table S1. Crystallographic data and structure refinement summary.[a]

Compound	**3**	**4**	**7**	**8**
CCDC number[b]	1447749	1447750	1447751	1447752
Molecular formula	$C_{20}H_{16}N_2O_2$	$C_{21}H_{16}N_2O_3$	$C_{21}H_{16}N_2O_3$	$C_{25}H_{18}N_2O$
Molecular weight	316.35	344.36	344.36	362.41
Crystal size / mm^3	0.35 × 0.29 × 0.04	0.46 × 0.27 × 0.24	0.44 × 0.19 × 0.17	0.27 × 0.16 × 0.13
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1$	P-1	$P2_1/c$	$P2_1/c$
a / Å	9.686(3)	11.240(1)	12.846(1)	10.436(1)
b / Å	10.175(3)	12.113(1)	17.232(1)	14.221(1)
c / Å	16.709(6)	13.506(1)	7.549(1)	12.880(1)
α / deg.	90.00	100.474(2)	90.00	90.00
β / deg.	102.177(5)	103.159(2)	96.393(1)	103.362(2)
γ / deg.	90.00	104.477(2)	90.00	90.00
V / Å^3	1609.7(9)	1677.2(2)	1660.7(3)	1859.8(3)
Z	4	4	4	4
$d_{calc.}$ / g cm^{-3}	1.305	1.364	1.377	1.294
μ / mm^{-1}.	0.086	0.753	0.760	0.626
λ / nm	0.71075	1.54184	1.54184	1.54184
Temperature / K	297(2)	298(2)	298(2)	298(2)
$2\theta_{max}$ / deg.	50.688	146.68	146.58	146.32
F_{000}	664	720	720	488
Measured/independent reflections	16626/5856	17108/6199	15853/3245	18110/3475
N_{para}	443	473	239	256
GOF	0.917	1.099	1.111	1.299
R_{int}	0.0418	0.046	0.0183	0.0156
R_1	0.0419	0.0729	0.0598	0.0925
wR_2 (all data)	0.0862	0.1948	0.1521	0.1836
Max/min residual electron density	0.118/-0.173	0.172/-0.240	0.203/-0.332	0.177/-0.288

[a,b] These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via *www.ccdc.cam.ac.uk/data_request/cif*.

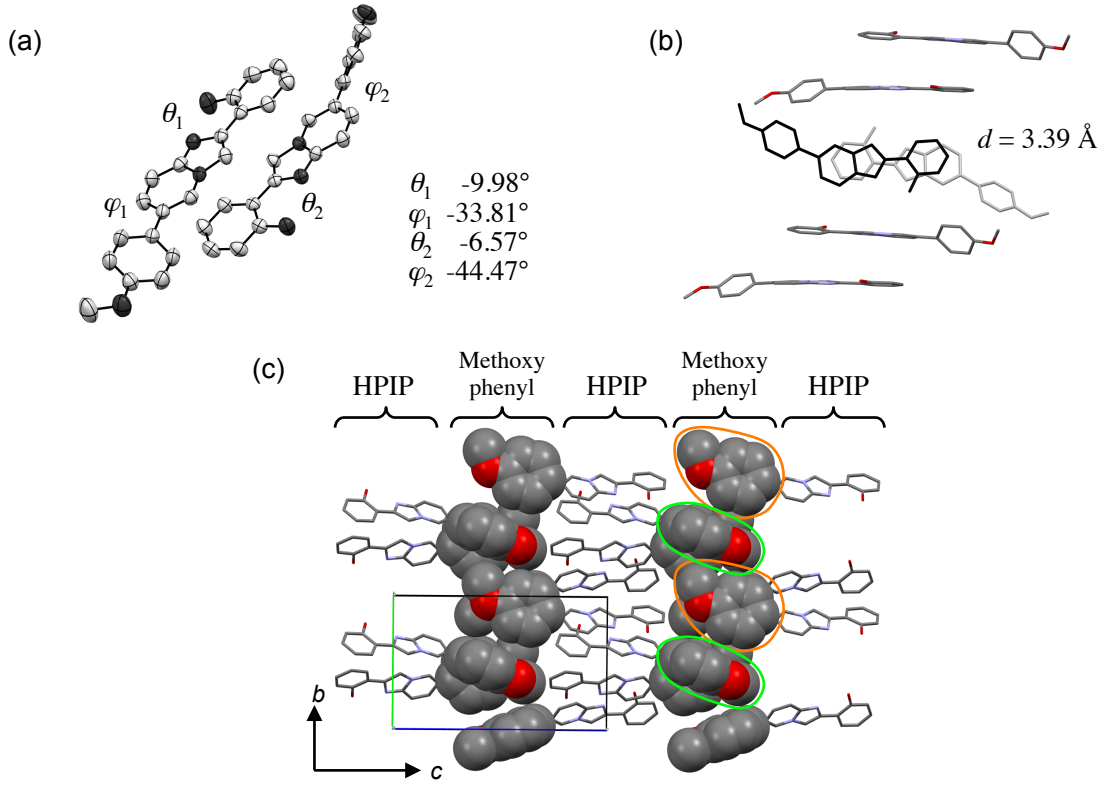


Figure S4. ORTEP drawings and molecular packing of **3**.

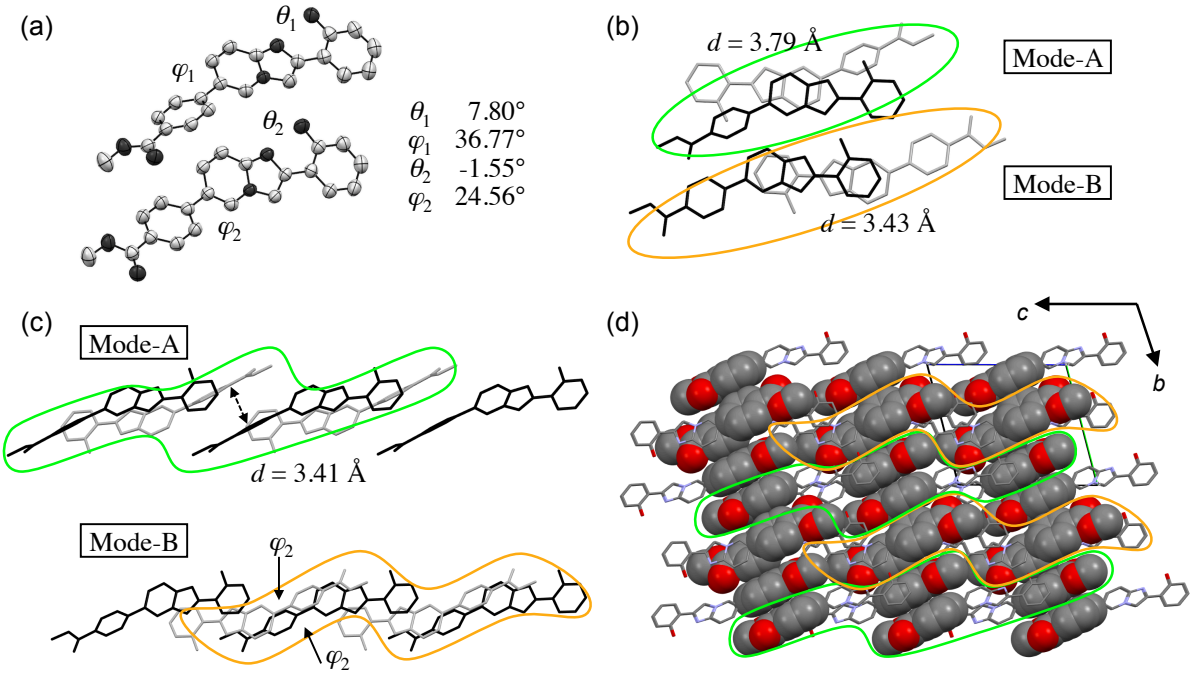


Figure S5. ORTEP drawings and molecular packing of **4**.

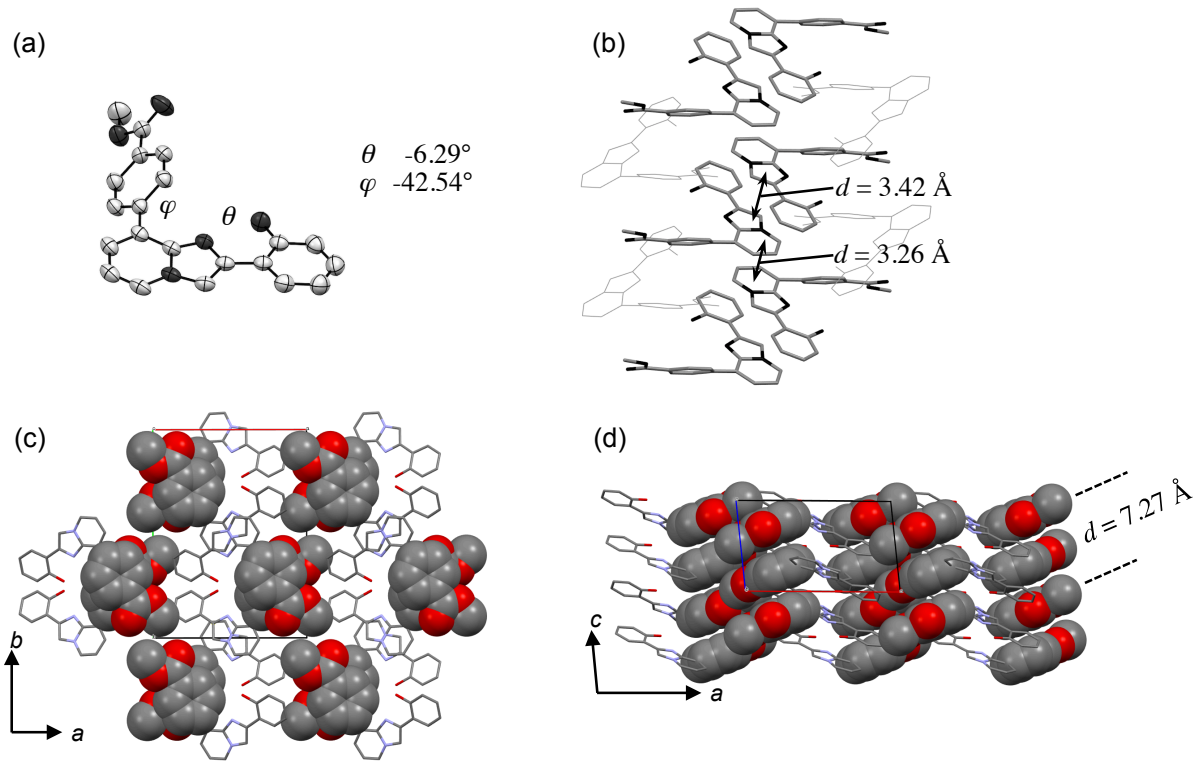


Figure S6. ORTEP drawings and molecular packing of **7**.

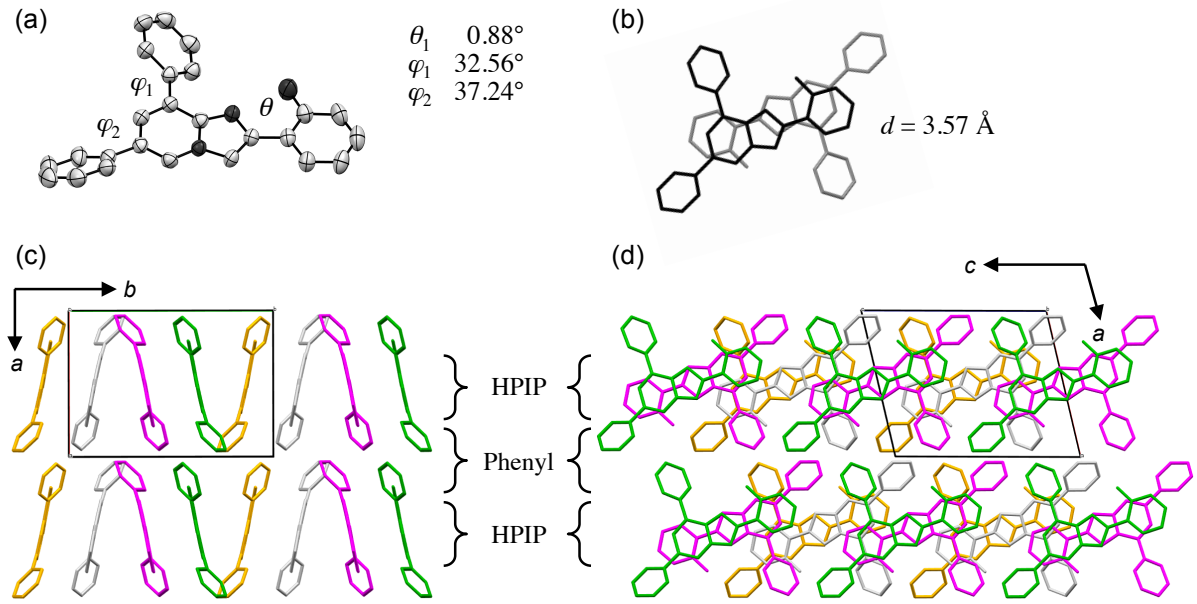


Figure S7. ORTEP drawings and molecular packing of **8**.