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Supporting Information(SI)

Synthesis and Aggregation induced emission property of novel boron-containing derivatives with Sensors for Viscous Alcohol-Fluids

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Synthesis



Scheme S1. The procedure for synthesis of compound A3 and A5-A7.

The procedures for synthesis of compound A1, A2 and A4 were according to the literatures [1].

Synthesis of compound A3

Compound 5-Bromo-9-ethoxy-1-oxophenalene, A1 (1.82 g, 6.0 mmol), 3-thiopheneboronic acid (0.92 g, 7.2 mmol), Pd(PPh₃)₄ (0.21 g, 0.18 mmol), NaHCO₃ (1.51 g, 18 mmol) was added into degassed THF (50 mL)/water (30 mL) under argon. Then the mixture was refluxed at 90 °C for 48

hours. After the solution cooled down, the mixture was extracted by CH₂Cl₂, and then obtained organic phase was washed by saturated aqueous NH₄Cl and dried by anhydrous Na₂SO₄. Then it was filtrated and concentrated to obtained crude product, which was purified (silica gel, petroleum ether/ethyl acetate 3:1, v/v) to give **A3** (1.38 g, 4.50 mmol) as a yellow powder, yield: 75.0 %. ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 8.19 (1H, d, *J* = 9.2 Hz), 8.13 (1H, d, *J* = 1.6 Hz), 8.03 (1H, d, *J* = 1.6 Hz), 7.73 (1H, d, *J* = 9.2 Hz), 7.61 (1H, q, *J* = 1.6 Hz), 7.53 (1H, q, *J* = 1.6 Hz), 7.50-7.47 (2H, m), 6.78 (1H, d, *J* = 9.6 Hz), 4.45 (2H, q, *J* = 7.2 Hz), 1.65 (3H, t, *J* = 7.2 Hz).

Synthesis of compound A5

Compound A2 (1.20 g, 4.0 mmol) and aniline (0.75 g, 8.0 mmol) was added in toluene (30 mL) and stirred and refluxed at 120 °C for 12 hours. Then the mixture was cooled down and excess solvent was removed to obtain crude product, which was purified (silica gel, petroleum ether/ethyl acetate 10:1, v/v) to give A5 (1.26 g, 3.64 mmol) as a red powder, yield: 91.0 %. ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 13.75 (1H, s), 8.11 (2H, d, *J* = 3.6 Hz), 7.97 (1H, d, *J* = 7.2 Hz), 7.94 (1H, d, *J* = 7.2 Hz), 7.73 (2H, d, *J* = 7.6 Hz), 7.54-7.45 (5H, m), 7.42-7.38 (3H, m), 7.30 (1H, t, *J* = 9.2 Hz), 7.05 (1H, d, *J* = 7.2 Hz). MS (ESI): calcd. for M = [C₂₅H₁₇ON]: 347.4; found: [M+1]⁺: 348.1.

Synthesis of compound A6

The method to synthesize compound A6 is similar with that of A5. Yield: 92.5 %.

¹H NMR (300 MHz, CDCl₃): δ [ppm] = 13.02 (1H, s), 8.25 (2H, d, *J* = 14.4 Hz), 8.15 (1H, d, *J* = 9.3 Hz), 8.07 (1H, d, *J* = 9.6 Hz), 7.75 (1H, d, *J* = 9.3 Hz), 7.40-7.63 (1H, m), 7.56-7.49 (4H, m), 7.46-7.41 (4H, m). MS (ESI): calcd. for M = [C₂₃H₁₅SON]: 353.4; found: [M+1]⁺: 354.1.

Synthesis of compound A7

The method to synthesize compound **A6** is similar with that of **A5**. Yield: 85.8 %. ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 13.75 (1H, s), 8.21 (2H, d, *J* = 3.6 Hz), 8.15 (1H, m), 8.00-7.84 (6H, m), 7.54-7.39 (7H, m), 7.29 (1H, t, *J* = 9.6 Hz), 7.06 (1H, d, *J* = 12.4 Hz). MS (ESI): calcd for: M = [C₂₉H₁₉ON]: 397.5; found: [M+1]⁺: 398.2.

Calculation analysis



Figure S1. A) Optimized molecular structures, and molecular orbital amplitude plots of HOMOs and LUMOs of compounds **3(a,b,c)** calculated using B3LYP/6-31G*.



Spectroscopic properties

Figure S2. A) Absorption spectra of 1c, 2c and 3c in THF solutions; B) Absorption spectra of 1c, 2c and 3c in solid film.



Figure S3. A) PL spectra of **1c-3c** in solid film, excited at maximum excitation wavelength, 395 nm. B) PL spectra of **3b** in THF/water mixtures with different water fraction (fw), excited at 468 nm.

Electrochemical analysis



Figure S4. Cyclic voltammograms of **1c-3c** in a dichloromethane solution of 0.1 molL⁻¹ Bu_4NPF_6 with a scan rate of 0.1 Vs⁻¹ and Fc/Fc⁺ as internal reference.

Optical and electrochemistry data

Table S1. Optical and electrochemistry data summary of compound 1a-3c.

λ ^{max} (nm) Solution ^a	λ ^{max} (nm) Film⁵	λ <mark>max</mark> FL (nm) Film ^c	HOMO ^d (ev)	LUMO ^d (ev)	Eg ^d (ev)	Eg ^d (ev)	𝒫 _F (%) Film
377,483	387,500	579	-6.05	-3.52	2.53	2.42	38
380,491	379,483	593	-5,86	-3.49	2.37	2.38	34
379,487	390,509	603	-5.89	-3.50	2.39	2.39	17
386,520	394,538	645	-5.26	-3.27	1.99	2 .11	74
387,503	399,543	635	-5.55	-3.51	2.04	2.08	69
386,500	391,537	643	-5.52	-3.50	2.20	2.09	73
383,506	388,525	644	-5.35	-3.34	2.01	2.10	81
382,502	390,533	636	-5.52	-3.50	2.02	2.07	70
385,523	389,525	646	-5.54	-3.47	2.07	2.09	67
	λ ^{max} (nm) Solution ^a 377,483 380,491 379,487 386,520 386,520 386,500 383,506 382,502 385,523	λ abs Solutionaλ max abs mb377,483387,500380,491379,483379,487390,509386,520394,538387,503399,543386,500391,537383,506388,525382,502390,533385,523389,525	λ abs Solutionaλ max Filmbλ Filmc377,483387,500579380,491379,483593379,487390,509603386,520394,538645387,503399,543635386,500391,537643383,506388,525644382,502390,533636385,523389,525646	λ abs Solutionaλ abs Filmbλ FilmcHOMOd (ev)377,483387,500579-6.05380,491379,483593-5.86379,487390,509603-5.89386,520394,538645-5.26387,503399,543635-5.55386,500391,537643-5.52383,506388,525644-5.35382,502390,533636-5.52385,523389,525646-5.54	λ abs Solutionaλ max Filmbλ FilmcHOMOd (ev)LUMOd (ev)377,483387,500579-6.05-3.52380,491379,483593-5.86-3.49379,487390,509603-5.89-3.50386,520394,538645-5.26-3.27387,503399,543635-5.55-3.51386,500391,537643-5.52-3.34383,506388,525644-5.35-3.34382,502390,533636-5.54-3.47	λ abs Solutionaλ abs Filmbλ FilmcHOMOd (ev)LUMOd (ev)Egd cv (ev)377,483387,500579-6.05-3.522.53380,491379,483593-5.86-3.492.37379,487390,509603-5.89-3.502.39386,520394,538645-5.26-3.271.99387,503399,543635-5.55-3.512.04386,500391,537643-5.52-3.342.01383,506388,525644-5.35-3.342.02385,523389,525646-5.54-3.472.07	λ abs Solutionaλ Filmbλ FilmcHOMOd (ev)LUMOd (ev)Egd (ev)Egd (ev)377,483387,500579-6.05-3.522.532.42380,491379,483593-5.86-3.492.372.38379,487390,509603-5.89-3.502.392.39386,520394,538645-5.26-3.271.992.11387,503399,543635-5.55-3.512.042.08386,500391,537643-5.52-3.342.012.10383,506388,525644-5.35-3.342.012.10382,502390,533636-5.52-3.502.022.07385,523389,525646-5.54-3.472.072.09

^a In THF solution (10 µm). ^b Film drop-casted on quartz plate. ^c Film drop-casted on quartz plate. ^d HOMO (/Fc) = -e (E^{l} , ox) + (-4.8) eV, LUMO (/Fc) = -e (E^{l} , re) + (-4.8) eV, $E_{g/cv}$ = LUMO-HOMO, $E_{g/opt}$ = 1240 / λ_{g} .

Reference

1 W. Yan, C. Hong, G. Long, Y. Yang, Z. Liu, Z. Bian, Y. Chen, C. Huang, Dyes Pigments 106 (2014) 197-204.