Supporting Information

Microcrystal Electron Diffraction Elucidates Water-Specific Polymorphism Induced Emission Enhancement of Bis-Arylaclyhydrazone

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1. Synthetic Procedures

**(N^1E,N^4E)-N^1,N^4-dibenzyldeneterephthalohydrazide (BAH-1).**

To a stirred solution of terephthalic dihydrazide (216 mg, 1.00 mmol) in MeOH (20 mL), benzaldehyde (0.219 mL, 2.10 mmol) was added. Purification after completion of the reaction afforded the desired product **BAH-1** (351 mg, 95%) as a white solid. **1H NMR** (500 MHz, DMSO-d6): δ 11.99 (s, 2H), 8.50 (s, 2H), 8.06 (s, 4H), 7.76 (d, J = 6.5 Hz, 4H), 7.54-7.41 (m, 6H); **13C NMR** (125 MHz, DMSO-d6): δ 162.4, 148.3, 136.1, 134.2, 130.2, 128.9, 127.8, 127.2; **UHRMS** (ESI) m/z calcd. for C_{22}H_{18}N_{4}O_{2}: 393.1328 ([M+Na]^+), found: 393.1325 ([M+Na]^+).

**(N^1E,N^4E)-N^1,N^4-bis(naphthalen-1-ylmethylene)terephthalohydrazide (BAH-2).**

To a stirred solution of terephthalic dihydrazide (100 mg, 0.463 mmol) in MeOH (9.3 mL), 1-naphthaldehyde (0.139 mL, 0.973 mmol) was added. Purification after completion of the reaction afforded the desired product **BAH-2** (187 mg, 86%) as a white solid. **1H NMR** (500 MHz, DMSO-d6): δ 12.10 (s, 2H), 9.15 (s, 2H), 8.90 (d, J = 8.5 Hz, 2H), 8.15 (s, 4H), 8.05 (t, J = 8.6 Hz, 4H), 7.97 (d, J = 7.1 Hz, 4H), 7.71 (t, J = 7.6 Hz, 2H), 7.64 (dd, J = 14.1, 6.7 Hz, 4H); **13C NMR** (175 MHz, DMSO-d6): δ 162.4, 148.2, 136.2, 133.6, 130.7, 130.3, 129.5, 128.9, 127.9, 127.9, 127.4, 126.4, 125.6, 124.2; **UHRMS** (ESI) m/z calcd. for C_{30}H_{22}N_{4}O_{2}: 493.1641 ([M+Na]^+), found: 493.1638 ([M+Na]^+).
(N'^1E,N'^4E)-N'^1,N'^4-bis(naphthalen-2-ylmethylene)terephthalohydrazide (BAH-3).

To a stirred solution of terephthalic dihydrazide (100 mg, 0.463 mmol) in MeOH (9.3 mL), 2-naphthaldehyde (155 mg, 0.973 mmol) was added. Purification after completion of the reaction afforded the desired product **BAH-3** (207 mg, 95%) as a white solid. **^1H NMR** (500 MHz, DMSO-d6): δ 12.10 (s, 2H), 8.66 (s, 2H), 8.19 (s, 2H), 8.11 (s, 4H), 8.07 - 7.91 (m, 8H), 7.59 (dd, J = 6.1, 3.2 Hz, 4H); **^13C NMR** (175 MHz, DMSO-d6): δ 162.4, 148.2, 136.2, 133.8, 132.8, 132.0, 128.8, 128.5, 128.3, 127.8, 127.7, 127.1, 126.7, 122.7; **UHRMS** (ESI) m/z calcd. for C_{30}H_{22}N_{4}O_{2}: 493.1641 ([M+Na]^{+}), found: 493.1637 ([M+Na]^{+}).

(N'^1E,N'^4E)-N'^1,N'^4-bis(4-methoxybenzylidene)terephthalohydrazide (BAH-4).

To a stirred solution of terephthalic dihydrazide (216 mg, 1.00 mmol) in MeOH (20 mL), p-anisaldehyde (0.261 mL, 2.10 mmol) was added. Purification after completion of the reaction afforded the desired product **BAH-4** (400 mg, 93%) as a white solid. **^1H NMR** (500 MHz, DMSO-d6): δ 11.85 (s, 2H), 8.43 (s, 2H), 8.04 (s, 4H), 7.70 (d, J = 8.6 Hz, 4H), 7.04 (d, J = 8.6 Hz, 4H), 3.82 (s, 6H); **^13C NMR** (175 MHz, DMSO-d6): δ 162.2, 161.0, 148.2, 136.2, 128.8, 127.7, 126.8, 114.4, 55.3; **UHRMS** (ESI) m/z calcd. for C_{24}H_{22}N_{4}O_{4}: 453.1539 ([M+Na]^{+}), found: 453.1537 ([M+Na]^{+}).

(N'^1E,N'^4E)-N'^1,N'^4-bis(4-tert-butylbenzylidene)terephthalohydrazide (BAH-5).

To a stirred solution of terephthalic dihydrazide (216 mg, 1.00 mmol) in MeOH (20 mL), 4-tert-butylbenzaldehyde (0.362 mL, 2.10 mmol) was added. Purification after completion of the reaction afforded the desired product **BAH-5** (419 mg, 87%) as a white solid. **^1H NMR** (500
MHz, DMSO-d6): \( \delta \) 11.92 (s, 2H), 8.46 (s, 2H), 8.05 (s, 4H), 7.68 (d, \( J = 8.3 \) Hz, 4H), 7.51 (d, \( J = 8.3 \) Hz, 4H), 1.31 (s, 18H); \(^{13}\)C NMR (175 MHz, DMSO-d6): \( \delta \) 162.4, 153.1, 148.3, 136.2, 131.5, 127.8, 127.0, 125.7; UHRMS (ESI) m/z calcd. for C\(_{30}\)H\(_{34}\)N\(_4\)O\(_2\): 505.2580 ([M+Na]\(^+\)), found: 505.2577 ([M+Na]\(^+\)).

\((N'^1E,N'^4E)-N'^1,N'^4\)-bis(4-fluorobenzylidene)terephthalohydrazide (BAH-6).

To a stirred solution of terephthalic dihydrazide (216 mg, 1.00 mmol) in MeOH (20 mL), 4-fluorobenzaldehyde (0.226 mL, 2.10 mmol) was added. Purification after completion of the reaction afforded the desired product BAH-6 (358 mg, 88%) as a white solid. \(^1\)H NMR (500 MHz, DMSO-d6): \( \delta \) 12.00 (s, 2H), 8.49 (s, 2H), 8.05 (s, 4H), 7.82 (dd, \( J = 8.3 \), 5.8 Hz, 4H), 7.32 (t, \( J = 8.7 \) Hz, 4H); \(^{13}\)C NMR (175 MHz, DMSO-d6): \( \delta \) 163.2 (d, \( J = 248.8 \) Hz), 162.4, 147.2, 136.1, 130.8 (d, \( J = 1.7 \) Hz), 129.3 (d, \( J = 8.5 \) Hz), 127.7, 115.9 (d, \( J = 22.0 \) Hz); UHRMS (ESI) m/z calcd. for C\(_{22}\)H\(_{16}\)F\(_2\)N\(_4\)O\(_2\): 429.1139 ([M+Na]\(^+\)), found: 429.1135 ([M+Na]\(^+\)).

\((N'^1E,N'^4E)-N'^1,N'^4\)-bis(thiophen-2-ylmethylene)terephthalohydrazide (BAH-7).

To a stirred solution of terephthalic dihydrazide (100 mg, 0.463 mmol) in MeOH (9.3 mL), thiophene-2-carboxaldehyde (0.0920 mL, 0.973 mmol) was added. Purification after completion of the reaction afforded the desired product BAH-7 (162 mg, 91%) as a pale yellow solid. \(^1\)H NMR (500 MHz, DMSO-d6): \( \delta \) 11.93 (s, 2H), 8.69 (s, 2H), 8.03 (s, 4H), 7.70 (d, \( J = 5.0 \) Hz, 2H), 7.50 (d, \( J = 3.2 \) Hz, 2H), 7.20-7.13 (m, 2H); \(^{13}\)C NMR (175 MHz, DMSO-d6): \( \delta \)
162.2, 143.4, 139.0, 136.1, 131.2, 129.2, 127.9, 127.7; **UHRMS** (ESI) m/z calcd. for C₁₈H₁₄N₄O₂S₂: 405.0456 ([M+Na]⁺), found: 405.0454 ([M+Na]⁺).

\( (N'^1E,N'^4E) - N'^1,N'^4\text{-bis((1H-indol-2-yl)methylene)terephthalohydrazide (BAH-8).} \)

To a stirred solution of terephthalic dihydrazide (216 mg, 1.00 mmol) in MeOH (20 mL), indole-2-carboxaldehyde (314 mg, 2.10 mmol) was added. Purification after completion of the reaction afforded the desired product BAH-8 (403 mg, 90%) as a yellow solid. **¹H NMR** (500 MHz, DMSO-d₆): δ 11.97 (s, 2H), 11.62 (s, 2H), 8.52 (s, 2H), 8.09 (s, 4H), 7.57 (d, \( J = 7.9 \) Hz, 2H), 7.46 (d, \( J = 8.1 \) Hz, 2H), 7.17 (t, \( J = 7.5 \) Hz, 2H), 7.02 (t, \( J = 7.4 \) Hz, 2H), 6.88 (s, 2H); **¹³C NMR** (175 MHz, DMSO-d₆): δ 162.2, 141.0, 138.0, 136.1, 133.1, 127.8, 127.6, 123.4, 120.8, 119.6, 112.1, 107.2; **UHRMS** (ESI) m/z calcd. for C₂₆H₂₀N₆O₂: 471.1545 ([M+Na]⁺), found: 471.1543 ([M+Na]⁺).
2. Supporting Figures

Figure S1. Images of solutions of BAHs (1.0 × 10^{-3} M in DMSO) under UV light (365 nm lamp).

Figure S2. Size of BAH-1 in DMSO/water co-solvent system (2.0 × 10^{-5} M in DMSO:water = 2:8) determined by DLS.
Figure S3. Absorption spectra of BAHs (dashed lines: $5.0 \times 10^{-6}$ M in DMSO, solid lines: $5.0 \times 10^{-6}$ M in DMSO/water with ratio of 2:8), a) BAH-1, b) BAH-2, c) BAH-3, d) BAH-4, e) BAH-5, f) BAH-6, g) BAH-7, h) BAH-8.
Figure S4. Simulated UV-Vis spectra of BAH-1 and BAH-1-H$_2$O (B3LYP and 6-311+G*).

Figure S5. Absorption spectra of BAH-1 (1.0 × 10$^{-6}$ M in DMSO and DMSO/water co-solvent with ratio of 3:7) and excitation profile recorded at 450 nm.
**Figure S6.** Emission spectra of BAH-1 ($2.0 \times 10^{-6}$ M) in DMSO/ethylene glycol (solid lines) plotted with BAH-1 in DMSO/water of same concentration (dashed line).

**Figure S7.** a) Absorption and b) emission spectra of BAH-1 in various co-solvent systems ($3.0 \times 10^{-6}$ M in DMSO/poor solvent = 2/8).
Figure S8. Emission spectra of wafer-1, wafer-2, and wafer-3 a) before and b) after fuming with solvent. c) Images obtained by optical microscope with samples used in b).

Figure S9. SEM images of BAH-1. Dispersed samples in MeOH (left) and H₂O (right) were drop-casted on glass slides.
**Figure S10.** Powder X-ray diffraction patterns of BAHs in the dried state (red) and water fumed state (blue).

**Figure S11.** Emission spectra of wafer-3 under vacuum and after rehydration. (PMT 700V)
Figure S12. Simulated FT-IR spectra of BAH-1 and BAH-1-H$_2$O (B3LYP and 6-311+G*).

Figure S13. The ORTEP diagrams for a) BAH-1-MeOH and b) BAH-1-H$_2$O with 50% thermal ellipsoid probability. 2D crystal packing arrangements of c) BAH-1-MeOH and d) BAH-1-H$_2$O complexes on the same planes in Fig. 3.
**Table S1.** Data collection and refinement statistics for BAH-1-H$_2$O and BAH-1-MeOH

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Figure S14. Hirshfeld surface of a) BAH-1-H$_2$O and b) BAH-1-MeOH mapped with shape index function.

Figure S15. Comparison of emission spectra of cryogenic cooled a) BAH-1-H$_2$O, b) BAH-1-MeOH, c) heated BAH-1-H$_2$O (in 100 °C vacuum oven, 2h) with the same samples under room temperature (22 ~ 25 °C). (PMT 300V)
**Figure S16.** Absolute PLQY of colloidal solutions of BAHs (1.0 × 10⁻⁵ M in DMSO:water = 2:8 (v/v)). Measurement conditions: PMT 360V, excited at absorption maxima.
3. $^1$H NMR and $^{13}$C NMR Spectra of New Compounds

Figure S17. $^1$H NMR spectrum of the compound BAH-1 (500 MHz, DMSO-$d_6$).

Figure S18. $^{13}$C NMR spectrum of the compound BAH-1 (125 MHz, DMSO-$d_6$).
Figure S19. $^1$H NMR spectrum of the compound BAH-2 (500 MHz, DMSO-$d_6$).

Figure S20. $^{13}$C NMR spectrum of the compound BAH-2 (175 MHz, DMSO-$d_6$).
Figure S21. $^1$H NMR spectrum of the compound BAH-3 (500 MHz, DMSO-$d_6$).

Figure S22. $^{13}$C NMR spectrum of the compound BAH-3 (175 MHz, DMSO-$d_6$).
Figure S23. $^1$H NMR spectrum of the compound BAH-4 (500 MHz, DMSO-$d_6$).

Figure S24. $^{13}$C NMR spectrum of the compound BAH-4 (175 MHz, DMSO-$d_6$).
Figure S25. $^1$H NMR spectrum of the compound BAH-5 (500 MHz, DMSO-$d_6$).

Figure S26. $^{13}$C NMR spectrum of the compound BAH-5 (175 MHz, DMSO-$d_6$).
Figure S27. $^1$H NMR spectrum of the compound **BAH-6** (500 MHz, DMSO-$d_6$).

Figure S28. $^{13}$C NMR spectrum of the compound **BAH-6** (175 MHz, DMSO-$d_6$).
Figure S29. $^{1}H$ NMR spectrum of the compound BAH-7 (500 MHz, DMSO-$d_6$).

Figure S30. $^{13}C$ NMR spectrum of the compound BAH-7 (175 MHz, DMSO-$d_6$).
Figure S31. $^1$H NMR spectrum of the compound BAH-8 (500 MHz, DMSO-$d_6$).

Figure S32. $^{13}$C NMR spectrum of the compound BAH-8 (125 MHz, DMSO-$d_6$).