Electronic Supplementary Information

N-type pyrazine and triazole-based luminogens with aggregation-enhanced emission characteristics

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Experimental Section

Materials: All commercially available chemicals were purchased from J&K, Across, Alfa Aesar or Sinopharm Chemical Reagent Co., Ltd unless specially stated and used as received without further purification. Cu(PPh₃)₃Br was prepared according to the literature procedures.¹ Pentadienylbis(triphenylphosphine)ruthenium(II) chloride [Cp*Ru(PPh₃)₂Cl] was purchased from Strem. 1-(6-Azidohexyloxy)benzene (**2**) was prepared according to our previous reported method.² THF was distilled from sodium benzopheone ketyl under dry nitrogen immediately prior to use.

Instrumentation: ¹H and ¹³C NMR spectra were recorded with a Bruker AV 300 or 400 spectrometer using $CDCl_3$ or $DMSO-d_6$ as solvent. The Fourier transform infrared (FT-IR) spectra were measure on a Perkin-Elmer 16 PC FT-IR Elemental analysis was performed on a ThermoFinigan Flash spectrophotometer. EA1112. UV-visible absorption spectra were measured on a Varian CARY 100 Biospectrophotometer. PL spectra were measured on a Perkin-Elmer LS 55 spectrofluorometer. Fluorescence quantum yields were estimated using quinine sulfate in 0.1 M H₂SO₄ as standard (54.6%). Cyclic voltammetry was carried out at room temperature in a three-electrode cell using CHI600D electrochemical workstation. Electrochemical investigations were conducted in anhydrous CH₂Cl₂ with a Pt disk as the working electrode, Pt wire as the auxiliary electrode, and SCE as a reference electrode. 0.1M *n*-tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte, and ferrocene was used as standard. The electrolyte solution was purged with nitrogen before electrochemical measurements, and the scanning rates were 50 mV s⁻¹. DSC and TGA were carried out with TA Q20 and TA Q 50 at a heating rate of 10 $^{\circ}C/$ min under N₂, respectively.

Synthesis of 1,2-bis(4-((trimethylsilyl)ethynyl)phenyl)ethane-1,2-dione (5): Into a 500 mL two-necked flask was added 60.5 mg (0.086 mmol) of Pd(PPh₃)₂Cl₂, 16.4 mg (0.086 mmol) of CuI, 11.2 mg (0.043 mmol) of PPh₃, 1.58 g (4.3 mmol) of 4,4'-

dibromobenzil, and a mixture of 240 mL of THF/triethylamine (2:1 v/v) under nitrogen. After the compounds completely dissolved, 1.7 mL (12 mmol) of (trimethylsiyl)acetylene was injected into the flask and the reactants were stirred at 50 °C for 24 h. After cooling down to room temperature, 130 mL of 4 M HCl was added to terminate the reaction. The mixture was extracted with dichloromethane (DCM) and the collected organic phases was washed with deionized water by three times and dried over anhydrous sodium sulfate. The filtrate was concentrated by a totary evaporator and the crude product was purified by a silica-gel column with DCM/hexane (1:5 by volume) as eluent. Yellow solid was obtained in 83.9% yield. IR (KBr), ν (cm⁻¹): 2980, 2156, 1683. ¹H NMR (400 MHz CDCl₃): δ (TMS, ppm) 7.90 (d, 4H), 7.59 (d, 4H), 0.28 (s, 18H). ¹³C NMR (100 MHz, CDCl₃): δ (TMS, ppm) 193.8, 133.1, 132.7, 130.6, 130.4, 104.3, 100.6, 0.42.

Synthesis of 1,2-bis(4-ethynylphenyl)ethane-1,2-dione (6): Into a 100 mL round bottom flask was added 50mL THF solution of 2 (1.4 g, 3.5 mmol) followed by slow injection of mixture of 9.8 mL (9.8 mmol) of tetrabutylammonium fluoride (TBAF, 1 M) THF solution and 0.57 mL (9.8 mmol) acetic acid. After striring for 1 h at room temperature, 50 mL deionized water was added and the mixture was extracted with 150 mL DCM by three times. The organic phase was washed by water three times and then dried over 5 g of anhydrous sodium sulfate for 1 h. The filtrate was condensed and purified by a silica-gel column with DCM/hexane (1:5 by volume) as eluent. Bronzing solid was obtained in 55.7% yield. IR (KBr), ν (cm⁻¹): 3273, 2980, 2126, 1672. ¹H NMR (400 MHz CDCl₃): δ (TMS, ppm) 7.95 (d, 4H), 7.64 (d, 4H), 3.34 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (TMS, ppm) 193.7, 133.3, 133.1, 130.4, 129.6, 83.1, 82.5.

Synthesis of 2,3-dicyano-5,6-bis(4-ethynylphenyl)pyrazine (1): Into a 250 mL round bottom flask was added 0.32 g (3 mmol) of diaminomaleonitrile (7), 0.5 g (1.94 mmol) of **6** and 125 mL acetic acid. After refluxing overnight, the mixture was cooled down to room temperature and then poured into 500 mL icy water. The precipitate was filtered and washed with water several times. The crude product was purified by a silica-gel column with DCM/hexane (2:5 by volume) as eluent. Faint yellow solid

was obtained in 68.8% yield. IR (KBr), ν (cm⁻¹): 3274, 2245, 2109. ¹H NMR (400 MHz CDCl₃): δ (TMS, ppm) 7.54 (m, 8H), 3.27 (s, 2H). ¹³C NMR (100 MHz, CDCl₃): δ (TMS, ppm) 155.0, 135.6, 133.3, 130.6, 130.4, 126.1, 113.6, 83.1, 81.2.



Synthesis of 1,4-isomer of 3a: Into a 10 mL Schlenk tube with a stopcock in the side arm was added 100 mg (0.3 mmol) of **1**, 145 mg (0.66 mmol) of **2**, 11.1 mg (0.012 mmol) of Cu(PPh₃)₃Br and 3 mL THF under nitrogen. After stirring for 20 h at 50 °C, the solvent was evaporated and the crude product was purified by a silica-gel column with ethyl acetate/hexane (1:2 by volume) as eluent. Yellow solid was obtained in 85.8% yield. IR (KBr), ν (cm⁻¹): 3127, 2951, 2245. ¹H NMR (400 MHz DMSO-*d*₆): *δ* (TMS, ppm) 8.68 (s, 2H), 7.92 (d, 4H), 7.64 (d, 4H), 7.25 (t, 4H), 6.9 (m, 6H), 4.42 (t, 4H), 3.92 (t, 4H), 1.89 (m, 4H), 1.70 (m, 4H), 1.45 (m, 4H), 1.32 (m, 4H). ¹³C NMR (100 MHz, CDCl₃): *δ* (TMS, ppm) 159.6, 155.3, 147.0, 135.2, 134.2, 131.2, 130.3, 130.1, 126.6, 121.3, 121.1, 115.1, 113.9, 68.1, 51.1, 30.9, 29.7, 26.9, 26.2. Anal. Calcd for: C₄₆H₄₄N₁₀O₂: C, 71.85; H, 5.77; N, 18.22; Found: C, 72.00; H, 5.86; N, 17.84.

Synthesis of 1,5-isomer of 3b: The synthetic procedure was similar to that of 3a except that the catalyst was replaced by Cp*Ru(PPh₃)₂Cl. White solid was obtained in 80.4% yield. IR (KBr), ν (cm⁻¹): 3127, 2951, 2245. ¹H NMR (400 MHz DMSO-*d*₆): δ (TMS, ppm) 7.96 (s, 2H), 7.68 (m, 8H), 7.24 (t, 4H), 6.89 (m, 6H), 4.44 (t, 4H), 3.832 (t, 4H), 1.69 (m, 4H), 1.55 (m, 4H), 1.28 (m, 4H), 1.16 (m, 4H). ¹³C NMR (100 MHz,

CDCl₃): δ (TMS, ppm) 159.5, 154.6, 136.9, 136.5, 134.1, 131.3, 131.1, 130.9, 130.1, 129.8, 121.3, 115.0, 113.5, 68.0, 49.1, 30.6, 29.6, 26.8, 26.0. Anal. Calcd for: C₄₆H₄₄N₁₀O₂: C, 71.85; H, 5.77; N, 18.22; Found: C, 71.86; H, 5.73; N, 18.30.



Figure S1. (A) DSC and (B) TGA curves of 3a and 3b recorded under a heating rate of 10°C/min under N₂



Figure S2. ¹H NMR spectrum of **5** in CDCl₃. The solvent peaks are marked with asterisks.



Figure S3. ¹³C NMR spectrum of **5** in CDCl₃. The solvent peaks are marked with asterisks.



Figure S4. ¹H NMR spectrum of 6 in CDCl₃. The solvent peak is marked with

asterisk.



Figure S5. ¹³C NMR spectrum of 6 in CDCl₃.



Figure S6. ¹H NMR spectra of (A) **1**, (B) **2**, (C) **3a** and (D) **3b** in CDCl₃. The solvent peaks are marked with asterisks.



Figure S7. ¹H NMR spectra of (A) 1, (B) 2, (C) 3a and (D) 3b in DMSO- d_6 . The solvent peaks are marked with asterisks.



Figure S8. ¹³C NMR spectra of (A) 1, (B) 2, (C) 3a and (D) 3b in CDCl₃. The solvent peaks are marked with asterisks.



Figure S9. PL spectra of **3b** in THF/water mixtures with different water fractions at room temperature. λ_{ex} = 346 nm, concentration = 10 µM.



Figure S10. Absorption spectra of (A) **3a** and (B) **3b** in THF/water mixtures with different water fractions at room temperature. Concentration = $10 \mu M$.



Figure S11. Cyclic voltammetry (CV) curves of **3a** and **3b** using ferrocene as standard.



Figure S12. Normalized PL spectra of TPA ($\lambda_{ex} = 290 \text{ nm}$), **3a** ($\lambda_{ex} = 367 \text{ nm}$) and **3a**/TPA complexes ($\lambda_{ex} = 380 \text{ nm}$) in their solid states.



Figure S13. PL spectra of **3b**/TPA complexes in their solid state. $\lambda_{ex} = 380$ nm.



Figure S14. Absorption spectra of (A) 3a/TPA and (B) 3b/TPA complexes in THF/water mixtures with different water fractions at room temperature. Concentration of the isomers and TPA = 10 μ M.



Figure S15. PL spectra of **3b**/TPA mixtures in THF/water mixtures with water fraction from 90 to 99%. λ_{ex} = 380 nm, concentration of **3b** and TPA = 10 μ M.



Figure S16. Normalized PL spectra of TPA (λ_{ex} = 290 nm), **3a** (λ_{ex} = 367 nm), **3b** (λ_{ex} = 346 nm), **3b**/TPA mixture (λ_{ex} = 380 nm) and **3b**/TPA mixture (λ_{ex} = 380 nm) films. The molar ratio of isomers/TPA in complexes = 1:1.

	$\lambda_{ m abs}$	$\lambda_{ m em, \ soln}$	$\lambda_{ m em, \ aggr}{}^a$	$E_{\rm HOMO}{}^b$	E_{LUMO}^{c}	$E_{g(opt)}^{d}$	
	[nm]	$[nm]/(\Phi_F)$	$[nm]/(\Phi_F)$	[eV]	[eV]	[eV]	
3a	367	474 (10.0)	474 (14.5)	-6.26	-3.28	2.98	
3 b	346	458 (1.8)	457 (6.8)	-6.56	-3.39	3.17	

Table S1. Optical and electronic properties of 3a and 3b.

^{*a*} Aggregates formed in THF/water mixtures with 99% water fraction. ^{*b*} Calculated according to the formula: $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g(opt)}}$. ^{*c*} Determined by CV measurement and calculated using ferrocene HOMO level: $E_{\text{LUMO}} = -$ (Ered onset- E(1/2) Fc/Fc+ + 4.8) eV, E(1/2) Fc/Fc+ = 0.42 eV. ^{*d*} Calculated from 1240/ λ_{edge} .

Table S2. Selected bond length (in Å), angles and dihedral angles (in deg) of **3a** and **3b** calculated using DFT/B3LYP/6-31G(d, p) basis set.

	1,4 -isomer	1,5-isomer
C ₂ -C ₃	1.480	1.483
C ₄ -C ₅	1.480	1.483
C ₈ -C ₉	1.465	1.469
C ₁₂ -C ₁₃	1.464	1.469
C ₇ -C ₈ -C ₉	119.89	119.60
C ₈ -C ₉ -N ₁₀	121.91	130.32
C_{11} - C_{12} - C_{13}	119.94	119.60
C ₁₂ -C ₁₃ -N ₁₄	121.95	130.32
$C_1 - C_2 - C_3 - C_4$	35.0	36.3
$C_3-C_4-C_5-C_6$	35.4	36.3
$C_7-C_8-C_9-N_{10}$	-0.8	-48.7
C ₁₁ -C ₁₂ -C ₁₃ -N ₁₄	1.6	-48.7

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