Electronic Supplementary Information (ESI) for

Keto-Salicylaldehyde Azine: Asymmetric Substituent Effect on Their Optical Property *via* Electron-donating Group Insertion

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1. General information

All the chemical reagents are purchased from commercial sources and directly used without further purification. ¹H NMR is measured on a Bruker AV 400Hz spectrometer in DMSO at room temperature. UV-vis absorption spectrum is measured on a Shimadzu UV-2600 spectrophotometer. PL spectra are recorded on a Horiba Fluoromax-4 spectrofluorometer.



Scheme S1 Synthetic route of N-DPAS, 2N-DPAS and 3N-DPAS

Synthesis of the intermediate diphenyl-hydrazine (M1) and N,N-diethyl-diphenylhydrazine (M2):

10g of diphenyl keto was dissolved in 200ml of ethanol, 20ml of hydrazine hydrate was added, and the mixture was heated under reflux for 3 hours. Slowly cooled to room temperature to obtain white needle crystals, which were recrystallized to give M1 10g. 10g of N,N-diethyl-diphenyl keto was dissolved in 200ml of ethanol, 20ml of hydrazine hydrate was added, and the mixture was heated under reflux for 3 hours. Cooled to room temperature to obtain white needle crystals, which were recrystallized to give M2 10g.

Synthesis of N-DPAS:

Take M1 1.96g (10mmol) and 1.34g (10mmol) of N,N-diethyl salicylaldehyde was placed in 100 ml of absolute ethanol and refluxed for 3 hours. Then, the ethanol was removed by a rotary evaporator and crystallization gave 3.0g (yield 95%) of N-DPAS pale yellow powder. ¹H NMR (400MHz, d-DMSO, ppm): 11.23 (s, 1H, -OH), 8.70 (s, 1H), 7.64-7.62 (m, 2H), 7.54-7.41 (m, 7H), 7.28-7.24 (m, 3H), 6.29 (d, 1H), 3.45 (m, 4H), 1.15(t, 6H); HRMS (C₂₄H₂₅N₃O): m/z 371.2343 (M+, calcd 371.1998).

Synthesis of 2N-DPAS:

Take M2 10mmol and salicylaldehyde 10mmol in 100ml of ethanol refluxed for 3 hours, and column chromatography to obtain 2N-DPAS pale yellow solid 3.0 g (yield 95%) product was 2N-DPAS. ¹H NMR (400 MHz, d-DMSO, ppm): 11.50 (s, 1H, -OH), 8.82 (s, 1H), 7.52-7.48 (m, 3H), 7.29 (t, 1H), 7.11 (d, 2H), 6.91 (t, 1H), 6.79 (d, 1H), 6.74-6.68 (m, 4H), 3.41-3.28 (m, 8H), 1.65-1.10 (m, 12H); HRMS ($C_{28}H_{34}N_4O$): m/z 442.2733 (M+, calcd 442.2733).

Synthesis of 3N-DPAS:

Take 10mmol of M2, 10mmol of N,N-diethyl salicylaldehyde and refluxed in 100ml of ethanol refluxed for 3 hours. The solvent was removed by a rotary evaporator and filtered to obtain 3.0g (yield 95%) of 3N-DPAS yellow powder. ¹H NMR (400 MHz, d-DMSO, ppm): 12.00 (s, 1H, -OH), 8.61 (s, 1H), 7.60 (d, 2H), 7.26-7.24 (m, 3H), 7.09 (d, 1H), 6.69-6.61 (m, 3H), 6.21 (d, 1H), 6.11 (s, 1H), 3.40-3.20 (m, 12H), 1.25-1.10 (m, 18H); HRMS ($C_{32}H_{43}N_5O$): m/z 513.3897 (M+, calcd 513.3468).



2. NMR spectra of N-DPAS, 2N-DPAS and 3N-SPAS

Figure S2 ¹H NMR spectra of 2N-DPAS



Figure S3 ¹H NMR spectra of 3N-DPAS

3. Photophysics data supplement

Solvation effect measurement:

 50μ L of a stock solution and 5mL of different solvents were mixed in a volumetric flask to conduct the absorption and fluorescence spectrum. The concentration of the test solution was 1.0×10^{-5} M. Here, Hexane, Toluene, Isopropanol, Tetrahydrofuran, Acetonitrile and Ethanol were chosen.

AIE performance measurement:

Aliquot 50 μ L stock solution was added to a 5.0 mL flask with different amounts of water and THF following our previous report for absorption and fluorescence spectrum. The concentration of the test solution was 1.0×10^{-5} M.

Metal ion selectivity measurement:

All the ClO- 4 salts of respective ions were dissolved in 5 mL aqueous solution according to their molecular weights (about 1mmol). The spectra of AIE dots without any ions were defined as "Blank" in 2.5 mL water containing 25 μ L stock solution, and the different metal ion (About 50 μ L) was added to the "Blank" for investigating the selectivity and anti-interference ability. Herein, Cu(ClO₄)₂, Hg(ClO₄)₂, AgClO₄, LiClO₄, NaClO₄, Zn(ClO₄)₂, Co(ClO₄)₂, Pb(ClO₄)₂, Mn(ClO₄)₂, Ni(ClO₄)₂, Ba(ClO₄)₂, Cd(ClO₄)₂, Mg(ClO₄)₂, Al(ClO₄)₃, Ca(ClO₄)₂ and Fe(ClO₄)₃ were chosen.



Figure S4 The Abs spectra of 2N-DPAS (A) and 3N-DPAS (B)



Figure S5 I/I_0 emission plots of N-DPAS (A), where I_0 is the PL intensity in pure THF solution; E, K (I/I_0 @465 nm and 521 nm) and E/K emission plots of 3N-DPAS (B, C), where I_0 is the PL intensity in pure THF solution (Insert: fluorescence image at f_w =0% and f_w =95%).



Figure S6 The histogram analysis of N-DPAS (A) and 3N-DPAS (C) dots upon addition of the mixture of Hg²⁺ and other ions, and 2N-DPAS (B) dots upon addition of the mixture of Cu²⁺ and other ions, where I_0 is the PL intensity of the naked probe at 535 nm, 548 nm and 558 nm (defined as "Blank"). (Red: Single ion effect; Green: Anti-interference ability for special ion)

Quantum yields (%)					
Hexane	Toluene	Isopropanol	THF	Acetonitrile	Ethanol
0.5	0.4	0.6	0.4	0.7	0.5
1.3	1.1	1.4	0.7	0.9	1.4
0.6	0.7	1.3	0.4	0.8	1.1
	Hexane 0.5 1.3 0.6	Hexane Toluene 0.5 0.4 1.3 1.1 0.6 0.7	Quantum y Hexane Toluene Isopropanol 0.5 0.4 0.6 1.3 1.1 1.4 0.6 0.7 1.3	Quantum yields (%) Hexane Toluene Isopropanol THF 0.5 0.4 0.6 0.4 1.3 1.1 1.4 0.7 0.6 0.7 1.3 0.4	Quantum yields (%) Hexane Toluene Isopropanol THF Acetonitrile 0.5 0.4 0.6 0.4 0.7 1.3 1.1 1.4 0.7 0.9 0.6 0.7 1.3 0.4 0.8

Table S1. The emission quantum yields of three compounds in different organic solvents.