

## Supporting Information

Effect of Regio-specific Arylamine Substitution on Novel  $\pi$ -extended Zinc Salophen Complexes: Density Functional and Time-dependent Density Functional Study Prompted for DSSC Applications

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### AUTHOR INFORMATION

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## SYNTHESIS

All chemicals used for synthesis were purchased from commercial vendors and were used directly without further purification. Tetrahydrofuran, dichloromethane, and methanol were dried in the distillation apparatus by means of Na (with benzophenone as indicator), CaH, and Mg (with I<sub>2</sub> as indicator), respectively and stored under nitrogen atmosphere before use.

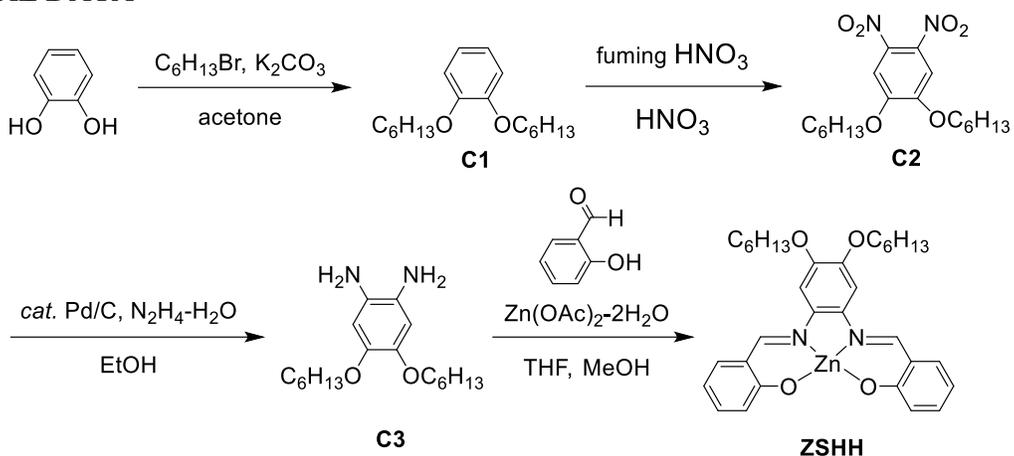
***1,2-bis(hexyloxy)benzene (C1)***. Catechol (1.246 g, 11.32 mmol) and potassium carbonate (3.936 g, 28.48 mmol) were mixed in acetone (50 mL) solution for 1 hour. The mixtures were added dropwise with 1-bromohexane (4 mL, 28.50 mmol), and the resulting solution was stirred at 80°C for 24 hours. After that, the solution was allowed to cooled to room temperature, and volatiles were removed under reduced pressure. The remaining residues were re-dissolved in CH<sub>2</sub>Cl<sub>2</sub> and washed with H<sub>2</sub>O for several times. The organic layer was collected, dried over MgSO<sub>4</sub>, and the volatiles were removed to give crude product as brown liquid. Further purification via column chromatography were conducted using silica gel (hexane as eluent) to give desired product **C1** as colorless liquid (yield 65%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.95–6.87 (m, 4H), 4.02 (t, *J* = 6.6 Hz, 4H), 1.85 (dt, *J* = 14.6, 6.6 Hz, 4H), 1.60–1.23 (m, 14H), 0.94 (dd, *J* = 8.5, 5.8 Hz, 7H).

***1,2-bis-hexyloxy-4,5-dinitro-benzene (C2)***. In a two-necked flask containing compound **C1** (2.30 g, 8.26 mmol), nitric acid (14 mL) were slowly added followed by dropwise addition of fuming nitric acid (1.2 mL) in an ice bath. The mixtures were stirred at 60°C for 12 hours. After that, the resulting solution were cooled to room temperature followed by poured into a copious of water. The yellow precipitates thus obtained were collected and washed with water several times. Further recrystallization with hexanes/CH<sub>2</sub>Cl<sub>2</sub> gives desired product **C2** as bright yellow powder (yield 96%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.29 (s, 2H), 4.10 (t, *J* = 6.5 Hz, 4H), 1.93 – 1.81 (m, 4H), 1.48 (dd, *J* = 14.8, 7.3 Hz, 4H), 1.36 (dt, *J* = 7.2, 4.9 Hz, 8H), 0.91 (t, *J* = 7.0 Hz, 6H).

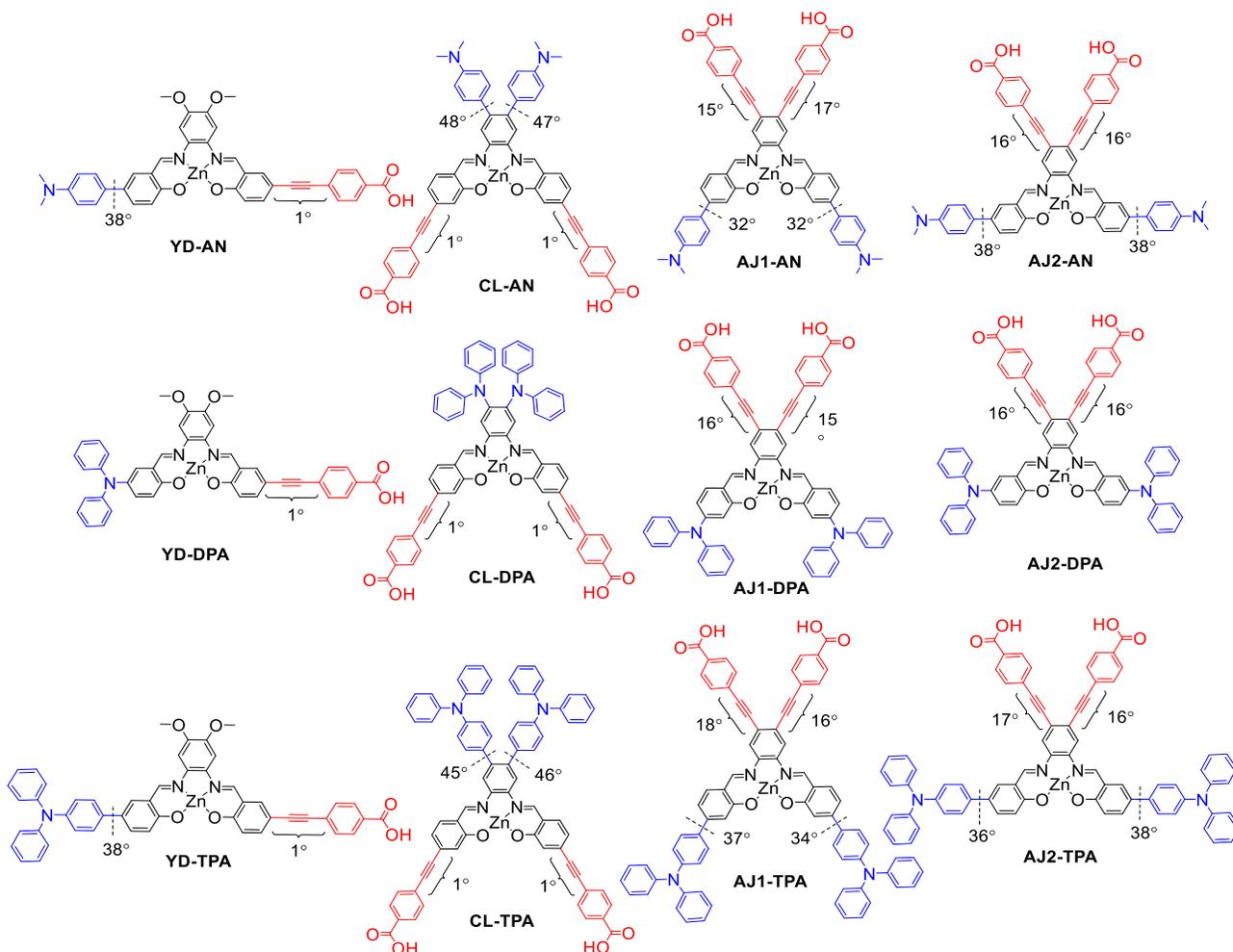
**1,2-bis-hexyloxy-4,5-diamine-benzene (C3).** Compound **C2** (1.119 g, 3.04 mmol) and Pd on activated carbon (5%, 79.5 mg, 0.0374 mmol) were weighted into a three-necked flask under nitrogen atmosphere. Ethanol (8 mL) and hydrazine monohydrate (3 mL) were syringed into the flask, and the resulting mixture were stirred at 80°C for 24 hours. After that, the resulting solution was cooled to room temperature, and the volatiles were removed under vacuum. The residues thus obtained were re-dissolved in CH<sub>2</sub>Cl<sub>2</sub> under nitrogen followed by filtered through Celite. The filtrate were evacuated with the aid of Schlenk system to gives white solid as **C3**. Since **C3** is unstable in air, it is used for further synthesis without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.38 (s, 2H), 3.89 (t, *J* = 6.6 Hz, 4H), 3.17 (s, 4H), 1.83 – 1.67 (m, 5H), 1.50 – 1.24 (m, 14H), 0.90 (dd, *J* = 9.0, 4.7 Hz, 7H).

**Compound ZSHH6.** Zinc acetate (0.323 g, 1.47 mmol) and salicylaldehyde (0.3 mL) were dissolved in a mixture of THF/MeOH (5 mL/10 mL) under nitrogen atmosphere for 30 minutes. The resulting mixture were added with a mixed solution of **C3** (10 mL/10 mL of THF/MeOH), and the resulting solution were stirred at room temperature for 24 hours. After that, volatiles of the solution were removed under vacuum, and the resulting residues were re-dissolved in CH<sub>2</sub>Cl<sub>2</sub>, recrystallized from methanol, and dried under vacuum to desired product **ZSHH6** as yellow powders (yield 86.4%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 8.95 (s, 2H), 7.47 (s, 2H), 7.42 (d, *J* = 6.1 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.51 (t, *J* = 7.4 Hz, 2H), 4.11 (t, *J* = 6.2 Hz, 4H), 1.76 (d, *J* = 8.1 Hz, 5H), 1.56 – 1.18 (m, 18H), 0.90 (t, *J* = 7.0 Hz, 8H). UV-Vis (10<sup>5</sup> M<sup>-1</sup> cm<sup>-1</sup> in THF): 356 (2.75), 411 (3.72), 445 (2.21).

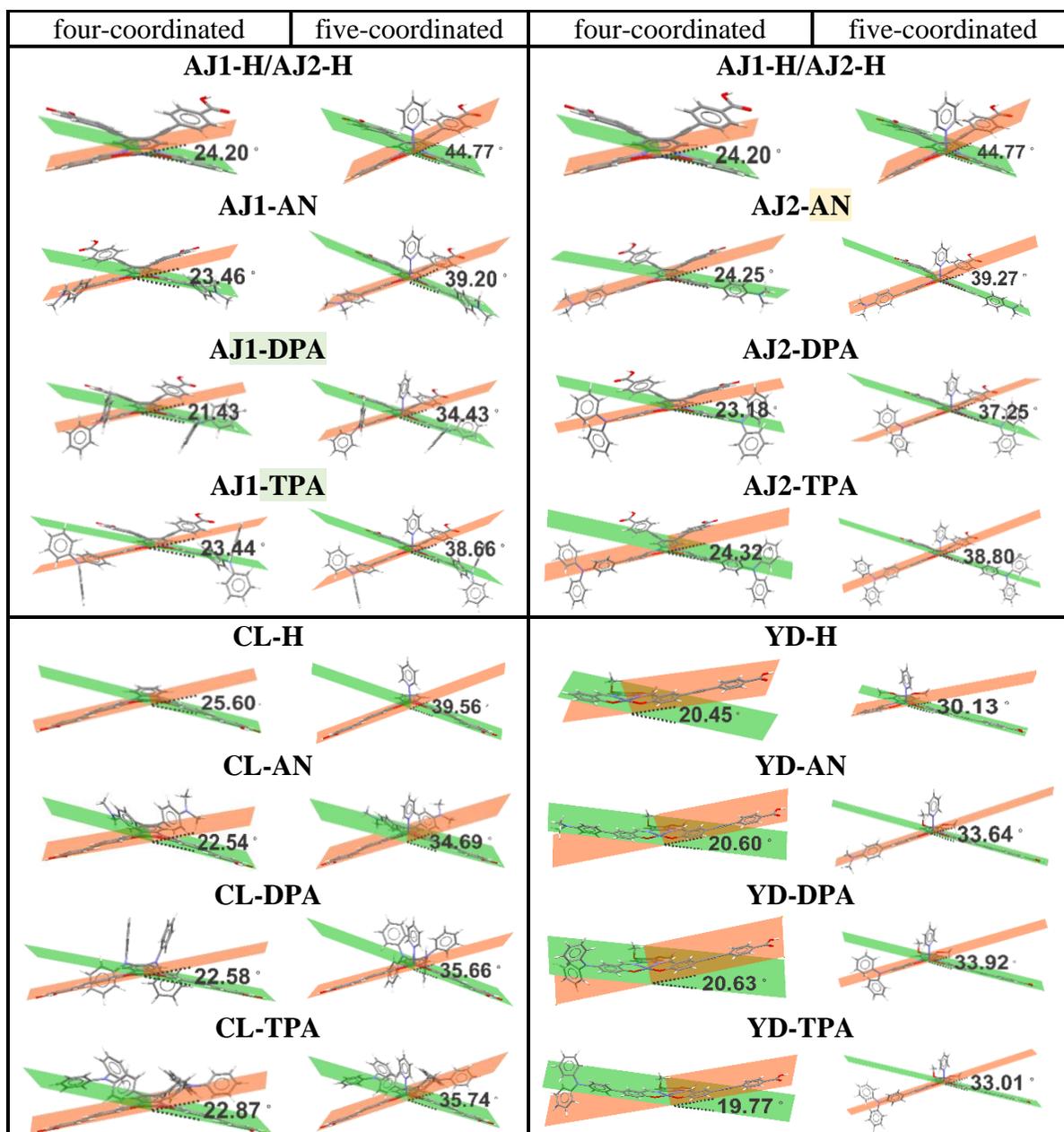
ADDITIONAL DATA



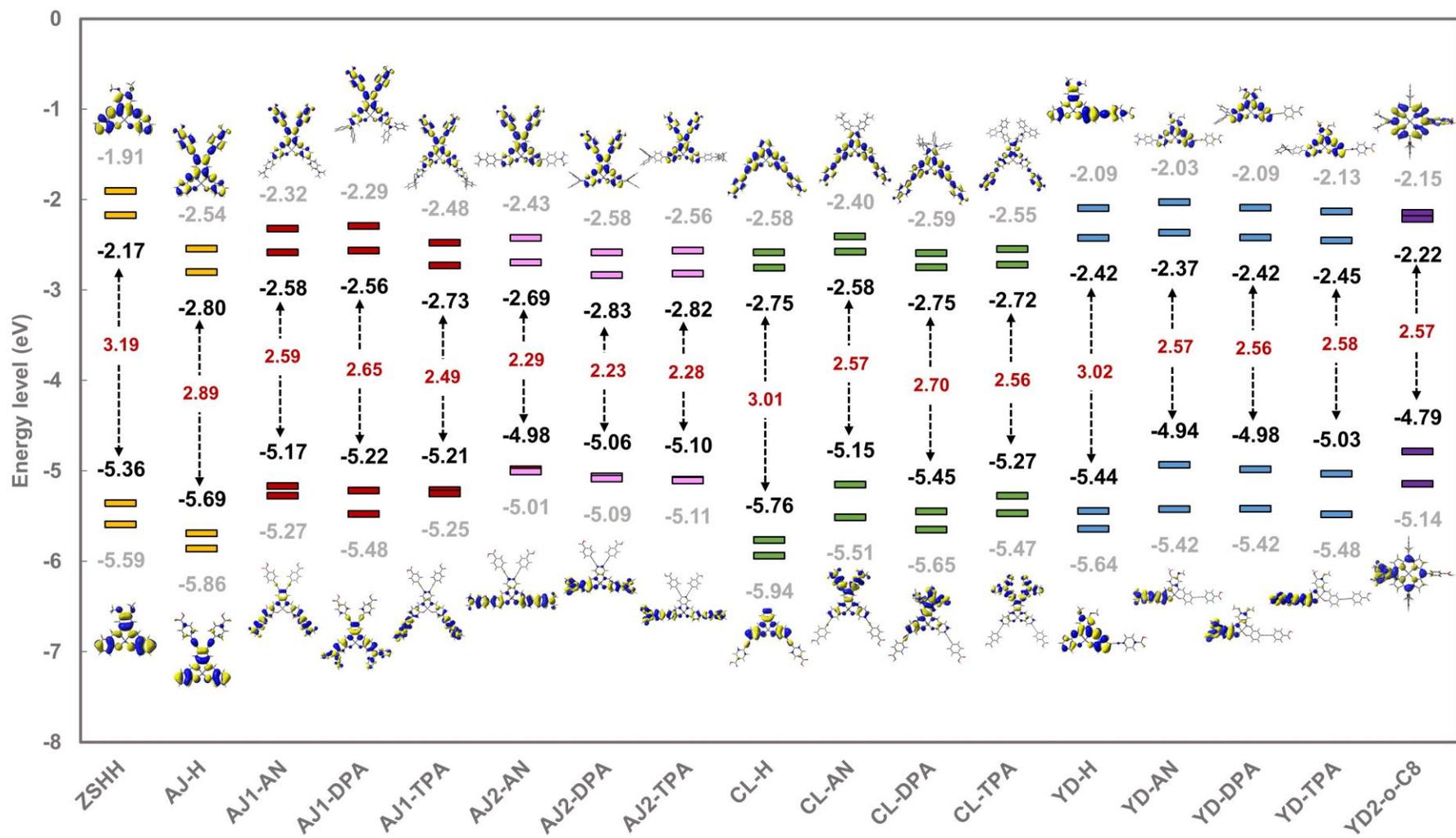
**Scheme S1.** Chemical synthesis of model compound **ZSHH6**.



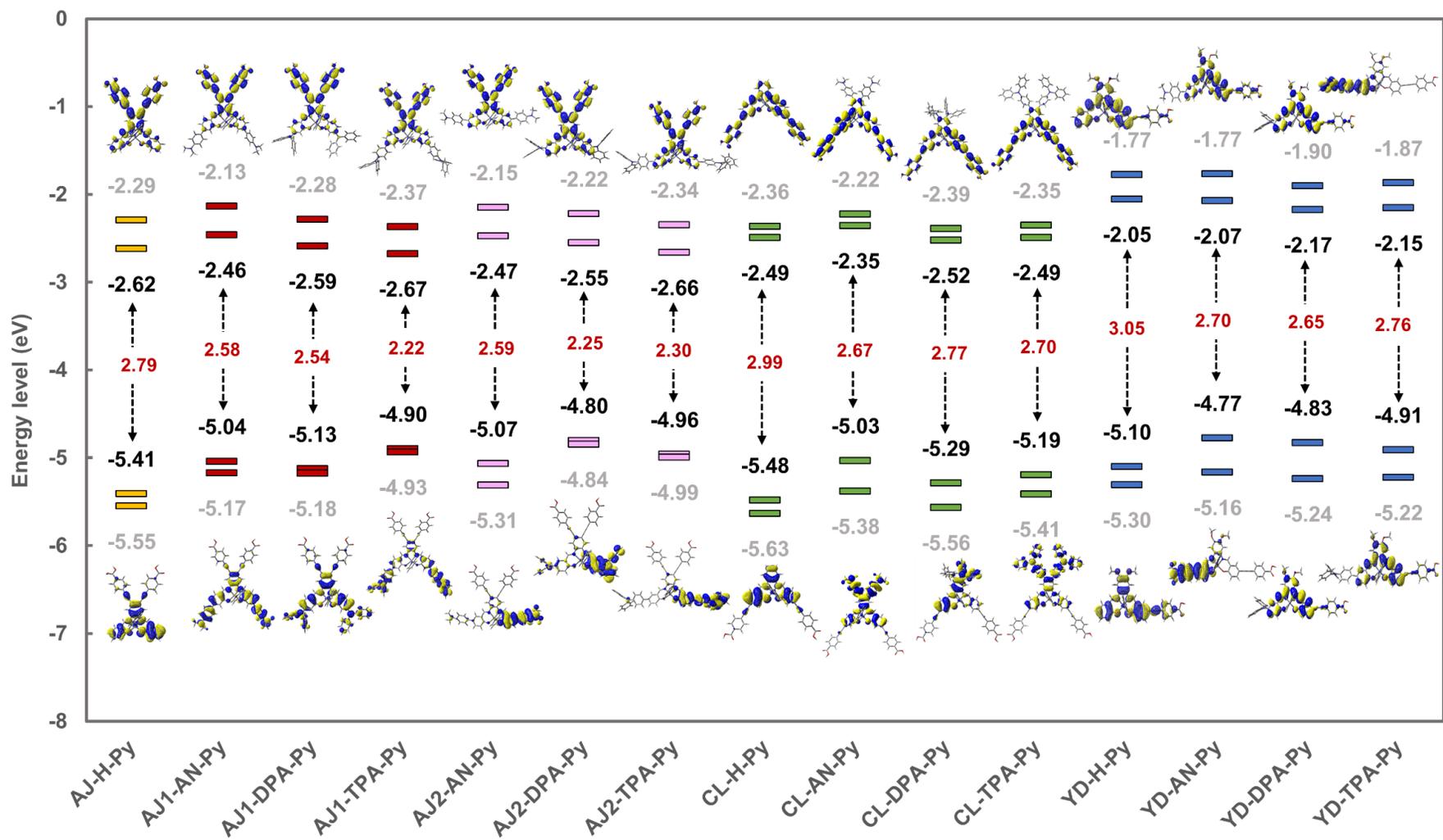
**Figure S1.** Calculated dihedral angles between each adjacent groups for the molecular geometries of ZSC dyes optimized at B3LYP/6-311G(d,p).



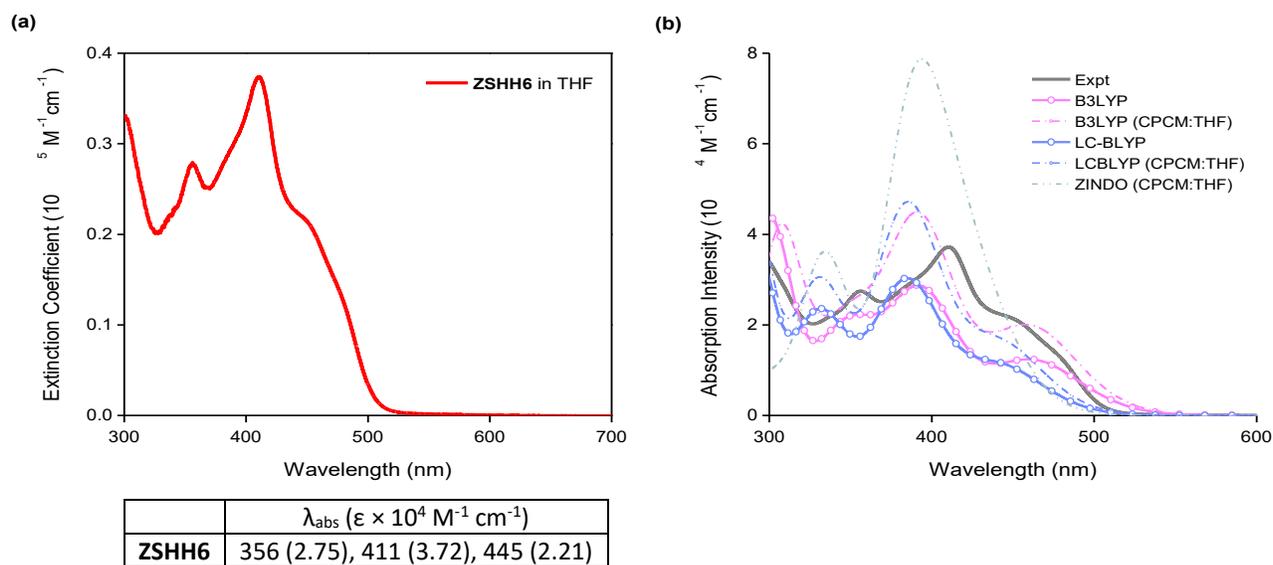
**Figure S2.** Out-of-plane distortion shown for four- and five-coordinated ZSC complexes optimized at B3LYP/6-311G(d,p). The angles were calculated by using the two phenoxides complexed to zinc center.



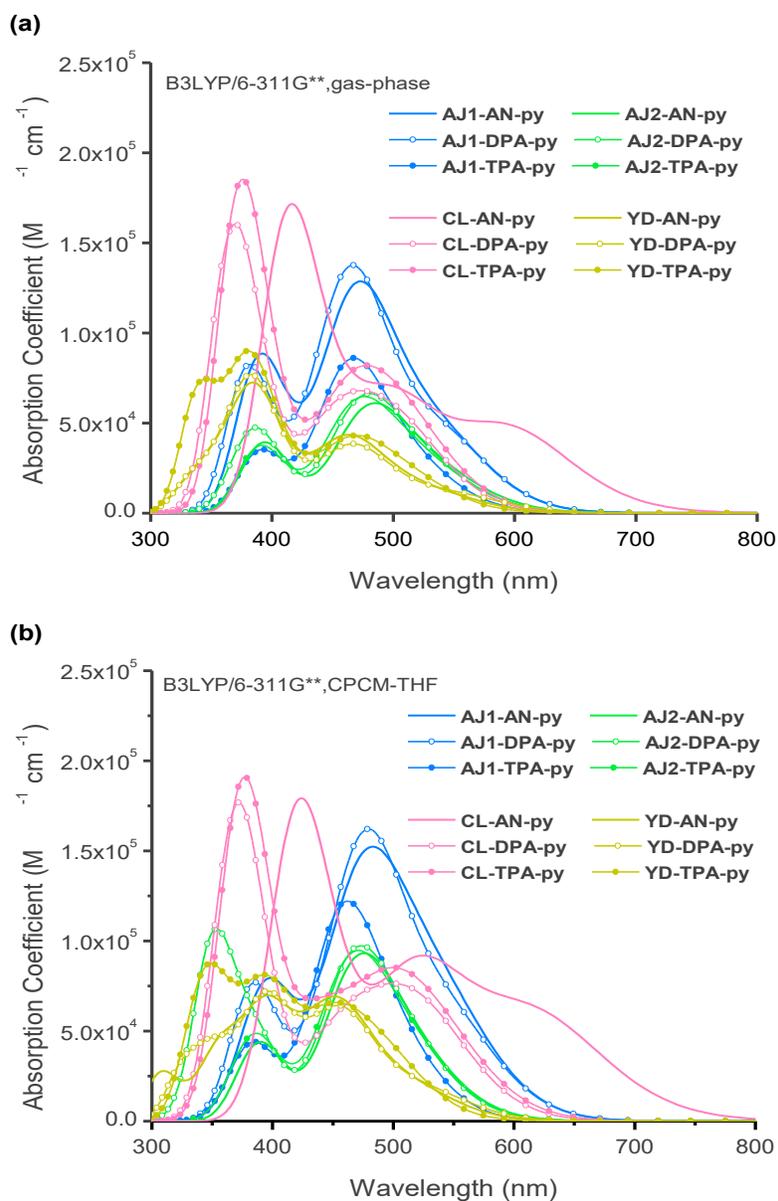
**Figure S3.** Energy level diagram for ZSC dyes and YD2-*o*-C8 with corresponding frontier molecular orbitals.



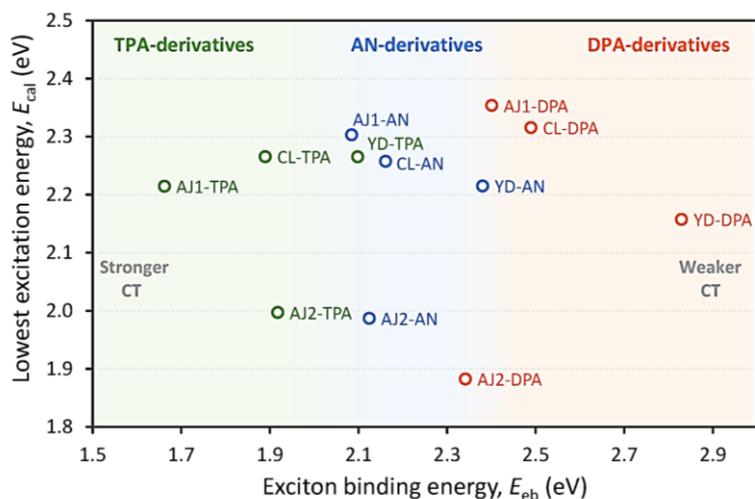
**Figure S3.** Energy level diagram for ZSC dyes and YD2-*o*-C8 with corresponding frontier molecular orbitals. (Continued)



**Figure S4.** (a) UV-Vis absorption spectra measured for **ZSHH6** in THF. (b) Comparison between experimental (gray line) and simulated UV-Vis absorption spectra for **ZSHH**. The 6-31G\* basis set were employed. Unless specified (dash-dotted line), all calculations were conducted in gas phase.

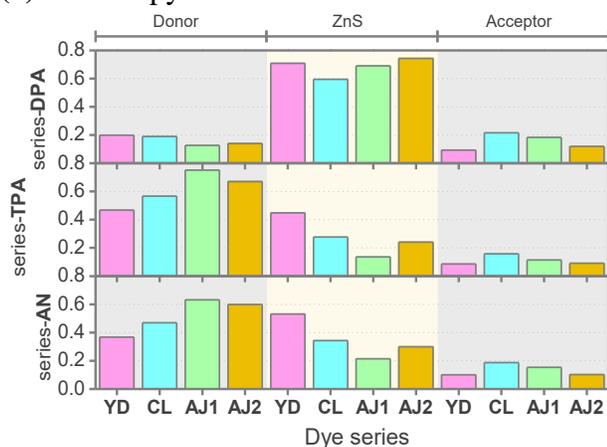


**Figure S5.** Simulated UV-Vis absorption spectra for pyridine-coordinated **YD-**, **CL-**, **AJ1-**, and **AJ2-** series dyes using 6-311G(d,p) basis set and (a) B3LYP as functional; (b) tuned LC-BLYP as functional.

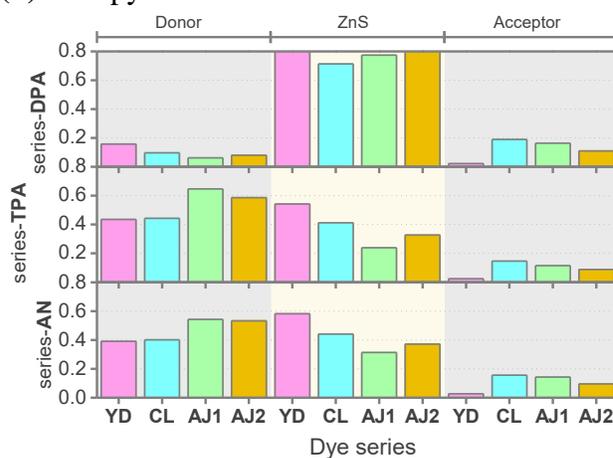


**Figure S6.** Plot of lowest-energy vertical excitation versus exciton binding energy.

**(a)** without pyridine coordination

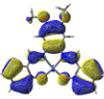
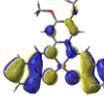
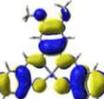
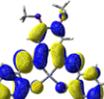
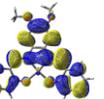
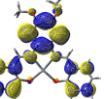
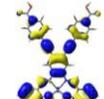
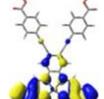
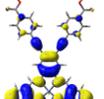
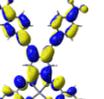
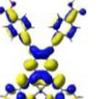
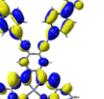
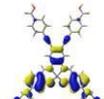
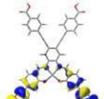
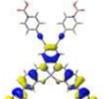
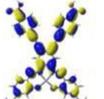
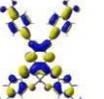
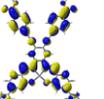
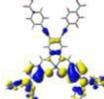
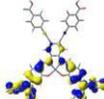
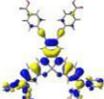
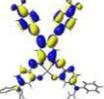
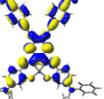
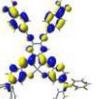
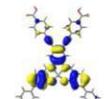
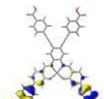
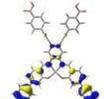
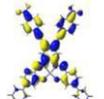
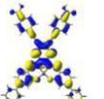
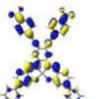
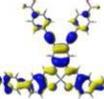
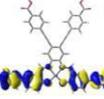
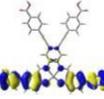


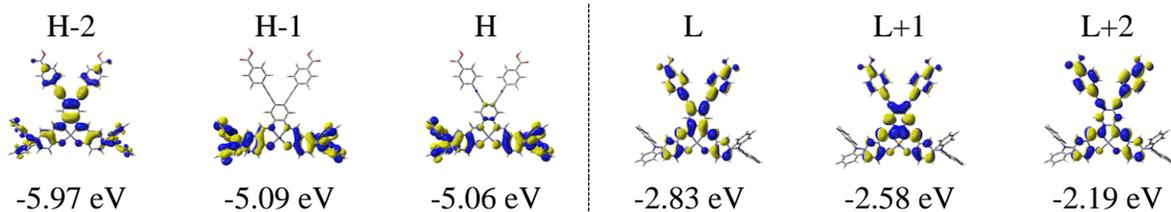
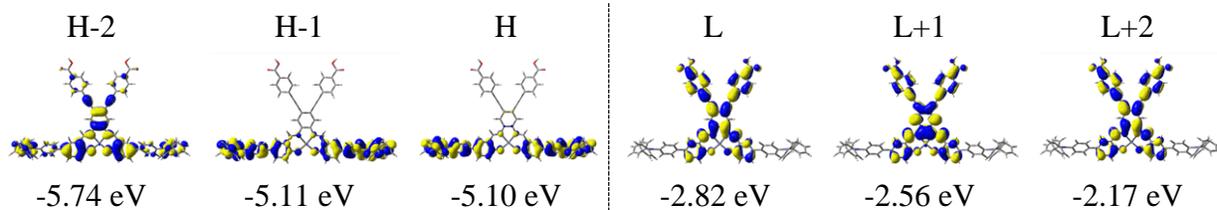
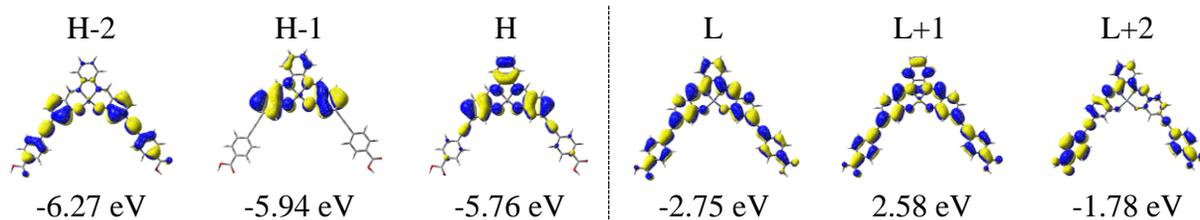
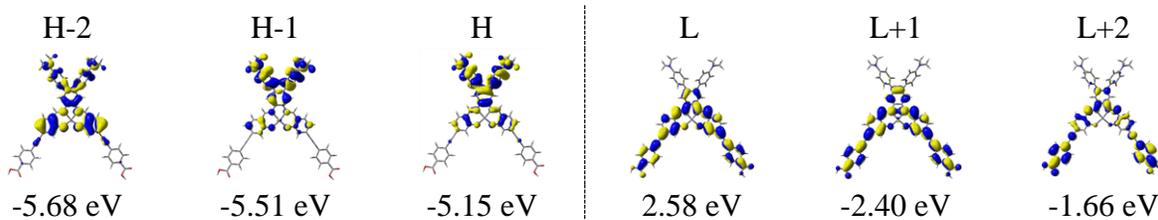
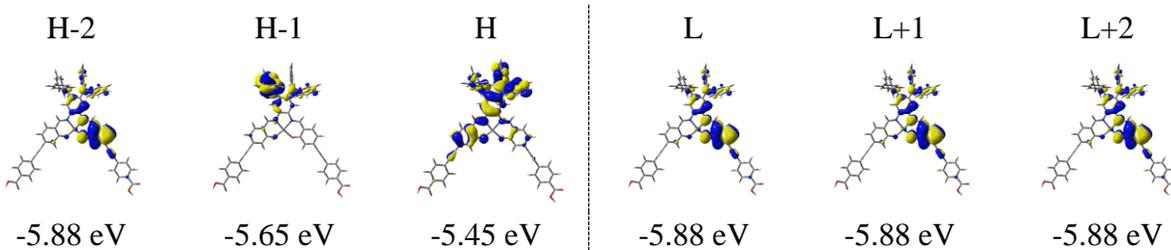
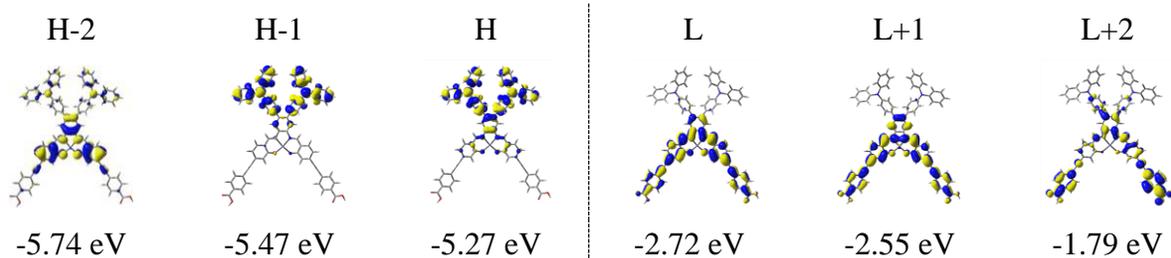
**(b)** with pyridine coordination

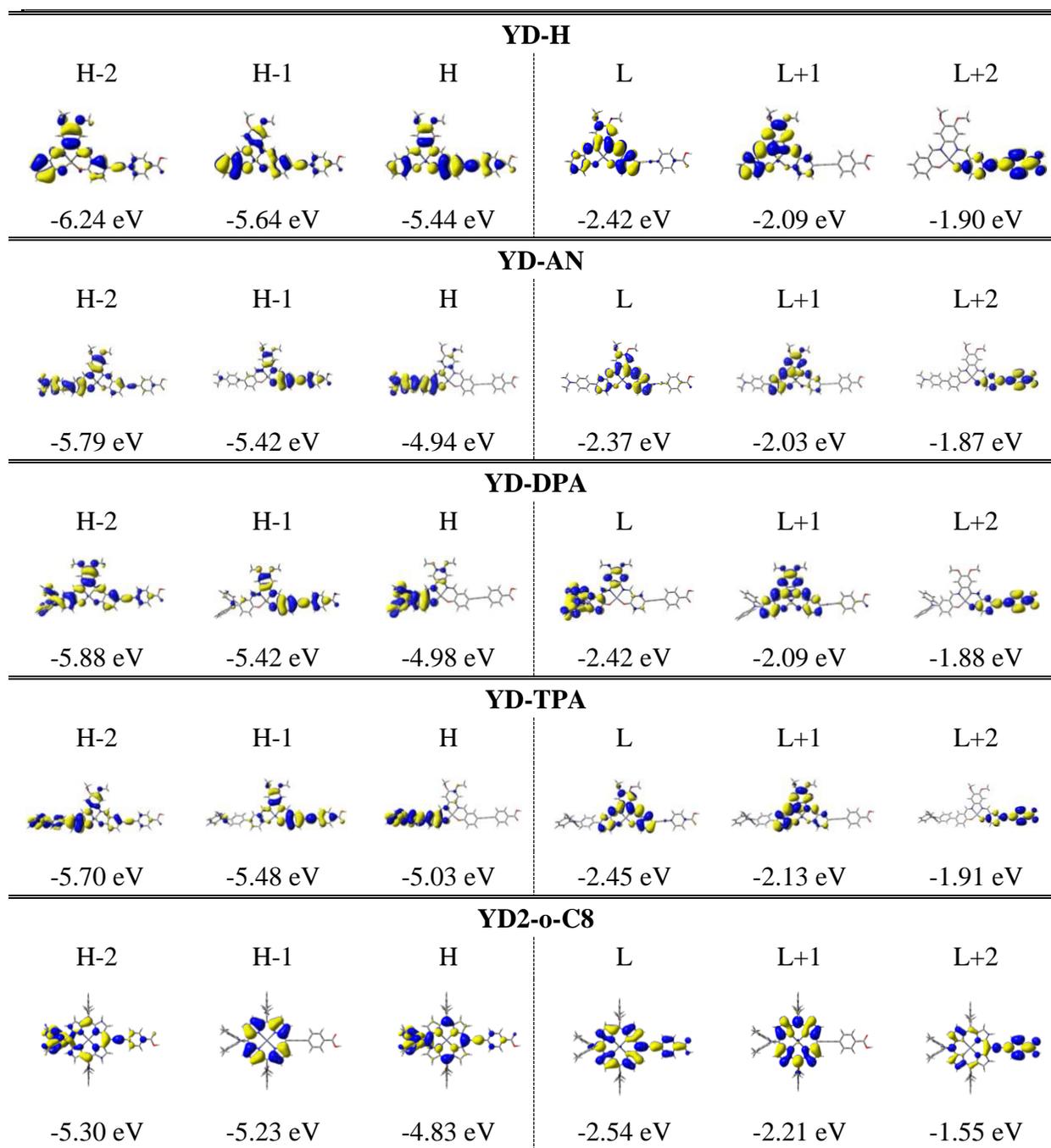


**Figure S7.** Mulliken charges for segments in YD-, CL-, AJ1- and AJ2-series dyes (a) without, and (b) with pyridine coordination, optimized at B3LYP/6-311G(d,p).

**Table S1.** Frontier molecular orbitals for compounds in this study.

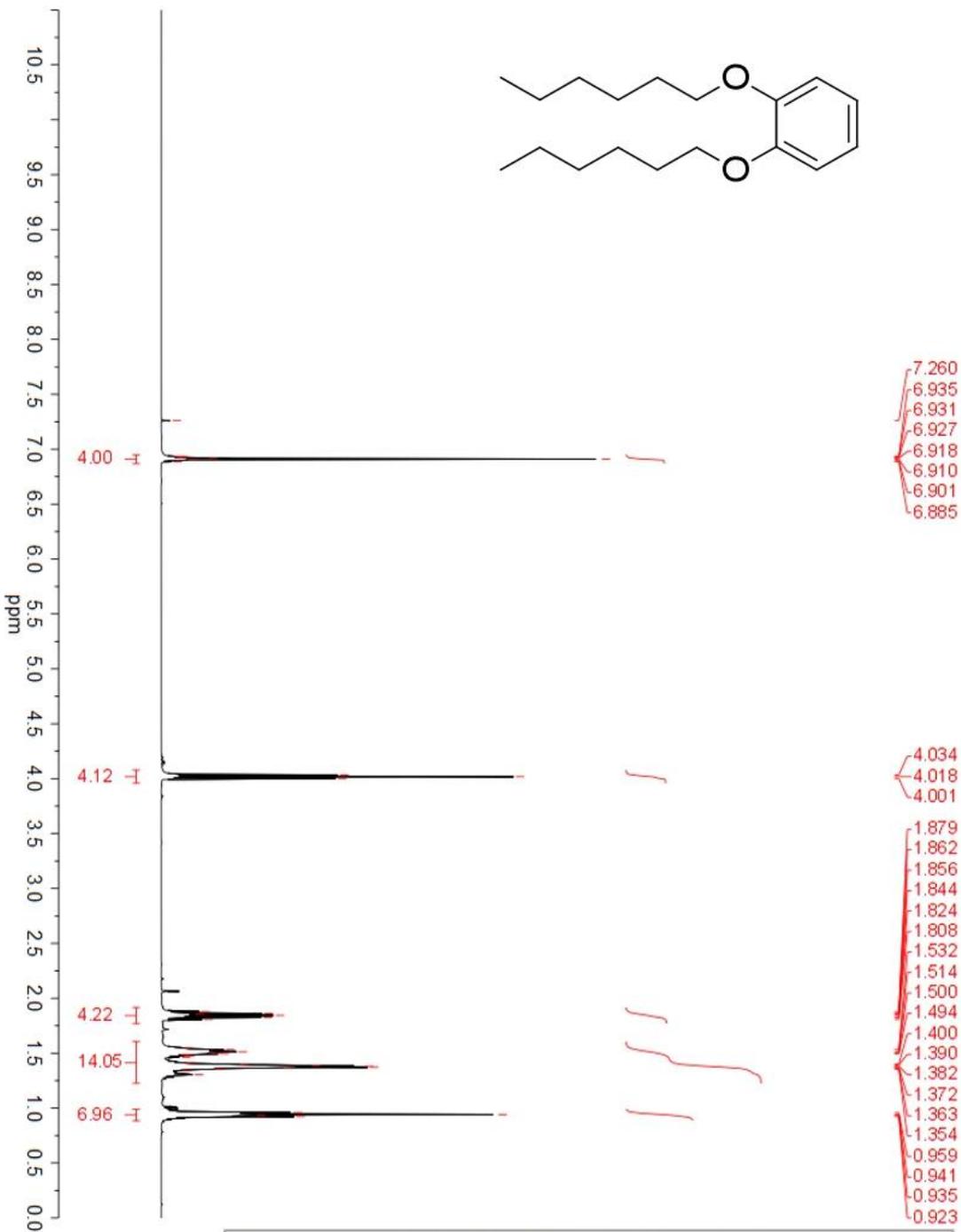
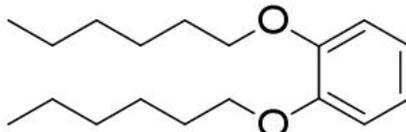
<b>ZSHH</b>					
HOMO-2	HOMO-1	HOMO	LUMO	LUMO+1	LUMO+2
					
-6.14 eV	-5.59 eV	-5.36 eV	-2.17 eV	-1.91 eV	-0.27 eV
<b>AJ1-H (AJ2-H)</b>					
H-2	H-1	H	L	L+1	L+2
					
-6.31 eV	-5.86 eV	-5.69 eV	-2.17 eV	-1.91 eV	-0.27 eV
<b>AJ1-AN</b>					
H-2	H-1	H	L	L+1	L+2
					
-5.50 eV	-5.27 eV	-5.17 eV	-2.58 eV	-2.32 eV	-1.97 eV
<b>AJ1-DPA</b>					
H-2	H-1	H	L	L+1	L+2
					
-5.69 eV	-5.48 eV	-5.22 eV	-2.56 eV	-2.29 eV	-1.93 eV
<b>AJ1-TPA</b>					
H-2	H-1	H	L	L+1	L+2
					
-5.61 eV	-5.25 eV	-5.21 eV	-2.73 eV	-2.48 eV	-2.12 eV
<b>AJ2-AN</b>					
H-2	H-1	H	L	L+1	L+2
					
-5.76 eV	-5.01 eV	-4.98 eV	-2.69 eV	-2.43 eV	-2.04 eV

**AJ2-DPA****AJ2-TPA****CL-H****CL-AN****CL-DPA****CL-TPA**



# NMR spectra of ZSHH6

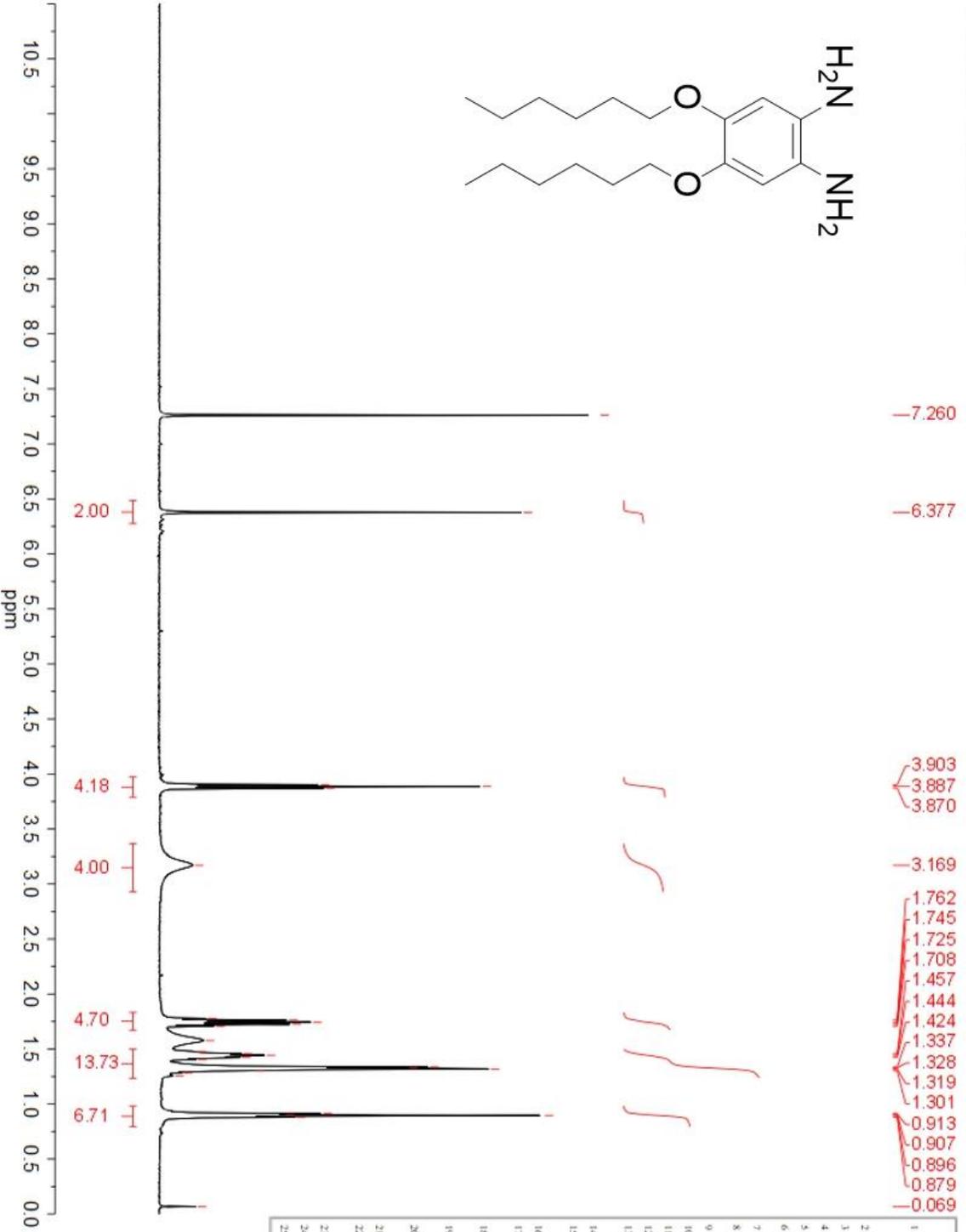
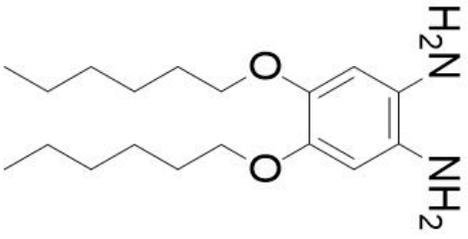
1,2-bis(hexyloxy)benzene (C1)



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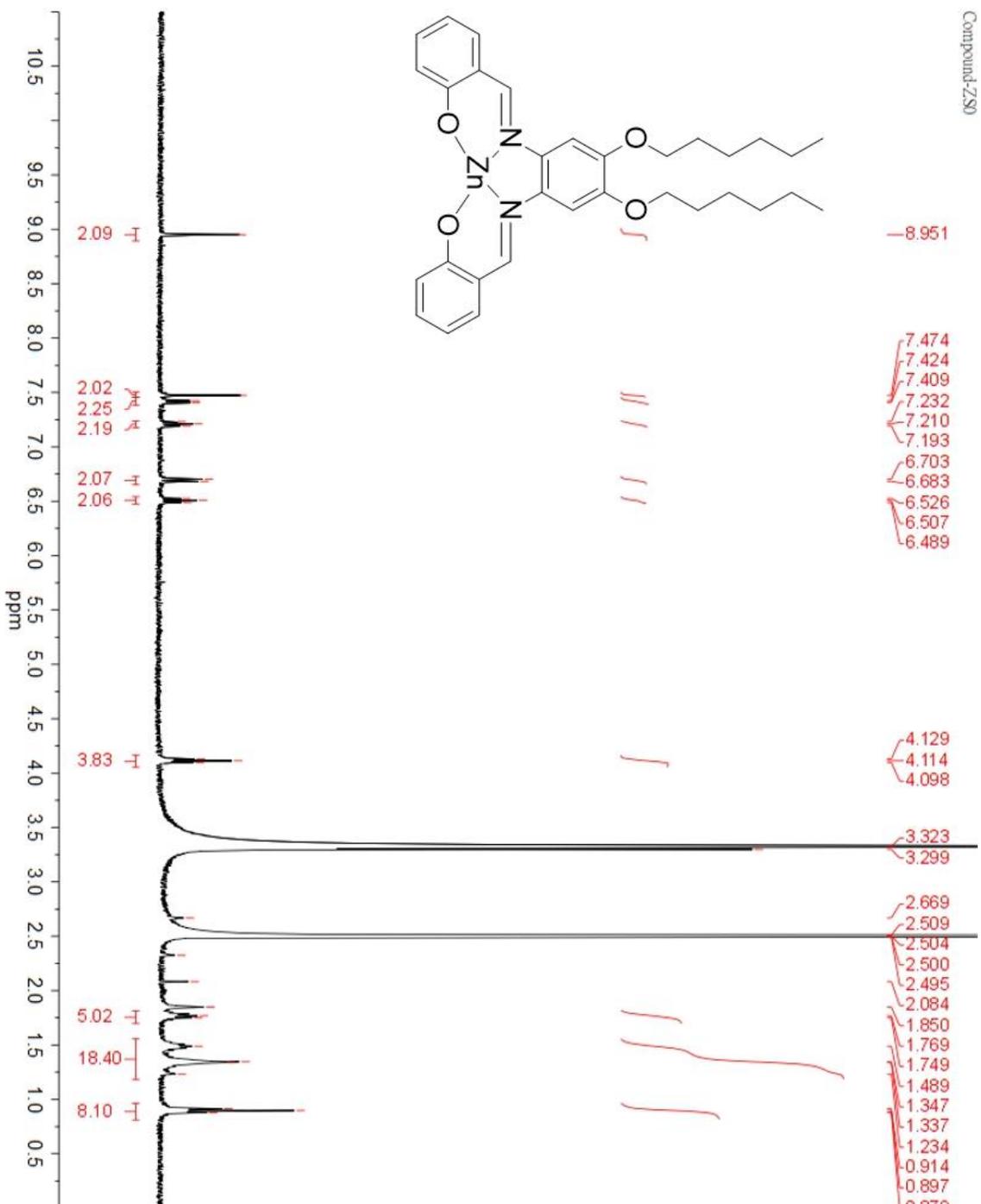
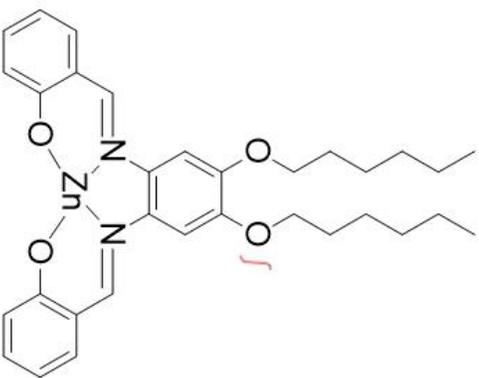


1,2-bis(hexyloxy)-4,5-diaminobenzene(C3).



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