Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Supporting Information

Photoluminescence of crystals of the isomers D-(−)-arabinose and L-(+)-arabinose, and insights into its mechanism

Qingfeng Wu[a], Chuchu Li[a], Xintong Li[a], Yuting Xiao[a], Qin Ding[a], Qing Zhou*[a,b,c]
[a] Qingfeng Wu, Chuchu Li, Xintong Li, Yuting Xiao, Qin Dinga, Dr. Q. Zhou

Engineering Research Center for Eco-Dyeing and Finishing of Textiles, Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Ministry of Education, College of Textile Science and Engineering (International Institute of Silk), Zhejiang Sci-Tech University, Hangzhou 310018, People's Republic of China

[b] Dr. Q. Zhou,

Zhejiang Sci-Tech University Shaoxing-Keqiao Research Institute, Building 8, Cross border E-commerce Park, Huashe Street, Keqiao District, Shaoxing City, Zhejiang, 312030, China

[c] Dr. Q. Zhou

Zhejiang Provincial Innovation Center of Advanced Textile Technology, Building 7, Cross border E-commerce Park, Huashe Street, Keqiao District, Shaoxing City, Zhejiang, 312030, China

Methods

Materials

D-(-)-Arabinos (D-Arb, 99%), L-(+)-Arabinos (L-Arb, 99%) and anhydrous ethanol (99.9%), which were purchased from Adamas-Beta Reagent Co. Purified water was purchased from Hangzhou Wahaha Group Co., Ltd and used as receive.

Purification of samples

D-(-)-Arabinose and L-(+)-Arabinose were initially dissolved in distilled water at room temperature, followed by the addition of ethanol (water/ethanol, v/v =1:20) to induce precipitation. The precipitate was collected via filtration through a sintered glass funnel and dried overnight in a vacuum oven at 40 °C.

Single crystal cultivation

Saturated aqueous solutions of D/L-Arb were made and placed in culture dishes for slow evaporation of water at room temperature.

Instrumentation.

^{1}H NMR spectra was obtained from AVANCE III HD 400MHz (Bruker BioSpin GmbH, Rheinstetten, Germany). The photoluminescence (PL) spectra of samples of the same quality were obtained with the fluorescence spectrophotometer (F-46001, Japan). Delayed PL spectra of solids at room temperature and phosphorescence lifetimes were measured on an Edinburgh FLS1000 fluorescence spectrometer. Photoluminescence quantum yields (PLQY) of solids were measured on Horiba FluoroMax-4 spectrophotometer equipped with Quanta-φ F-3029 integrating sphere. . Crystallography data for D-Arb and L-Arb were collected on a Bruker D8 Venture-CMOS diffractometer with CuK X-ray source radiation (λ = 1.54184 Å) at room temperature in the ω scan mode.Luminescent photographs and the videos were recorded using acamera (Sony A7S2, Japan) and the afterglow images were captured from the videos.

Computational study

ORCA5.0.3program[1] was utilized to perform the DFT calculations with this fundamentals and functionals (!B3LYP D3 def2-TZVP(-f) def2/J RIJCOSX). The frontier molecular orbitals (FMO) were obtained via Multiwfn (Version 3.8(dev))[2, 3] and VMD version 1.9.3 (November 30, 2016)[4] .

Methods of Ab initio molecular dynamics (AIMD): AIMD simulations of this system were calculated at the B97−3c level with ORCA 5.0.3, and the dynamic trajectories were visualized by VMD software. 2000 fs trajectories of D/L-Arb dimers were simulated at 298.15 K. The variation of dynamic distance between oxygen atom can be shown by VMD.

Calculation criteria for H-bonds: (1) The distance of X-H···Y should be less than 3.5 Å; (2) The angle between X-H in the hydrogen bond donor and Y on the hydrogen bond acceptor should be <30 degrees.

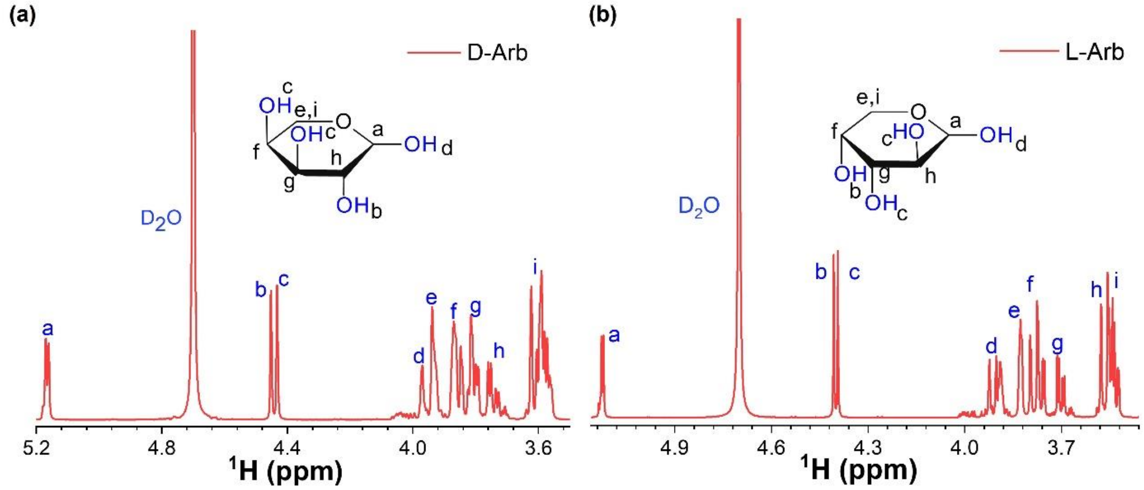

Fig. S1 ^{1}H NMR of (a)D-Arb and (b)L-Arb.

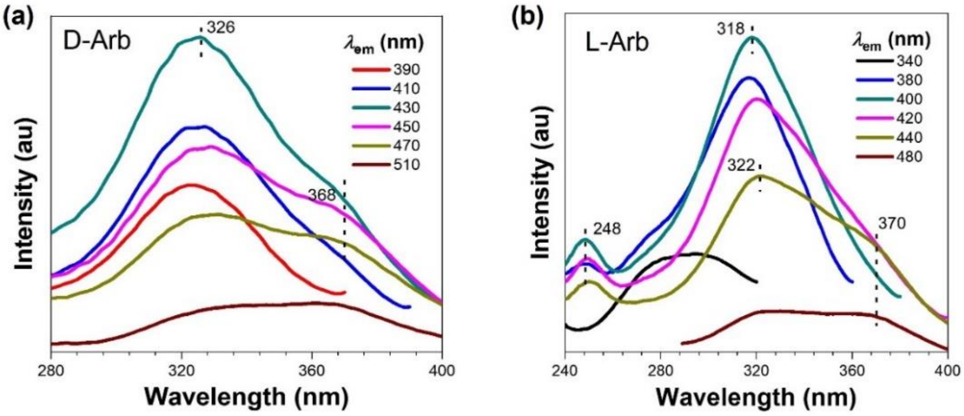

Fig. S2 Excitation spectra of (a)D-Arb and (b)L-Arb crystals under different λ_{em}

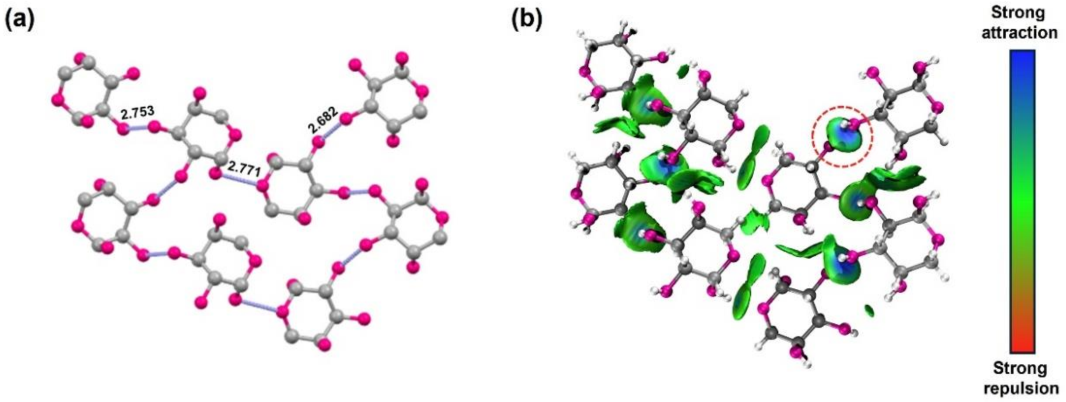

Fig. S3 (a)Single-crystal structure fragmental molecular packing with denoted intermolecular short contacts among electron-rich units of L-Arb. (b) NCI plots of L-Arb

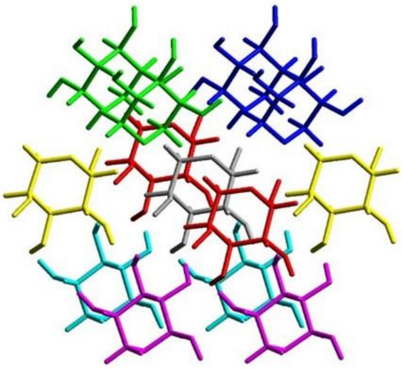

Fig. S4 Cluster of L-Arb extracted from its single-crystal structure Molecules are colored according to their pairwise interaction with the central molecule (colored grey).

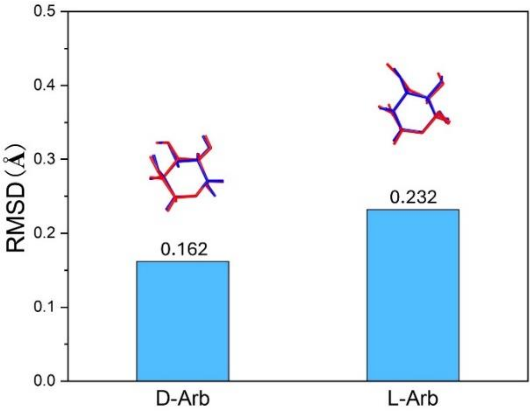

Fig. S5 The RMSD values of the atomic positions were calculated to evaluate the strength of intramolecular motion in two different states (ground-state (blue colour) and excited-state S1 (red colour) geometries of D/L-Arb molecule.

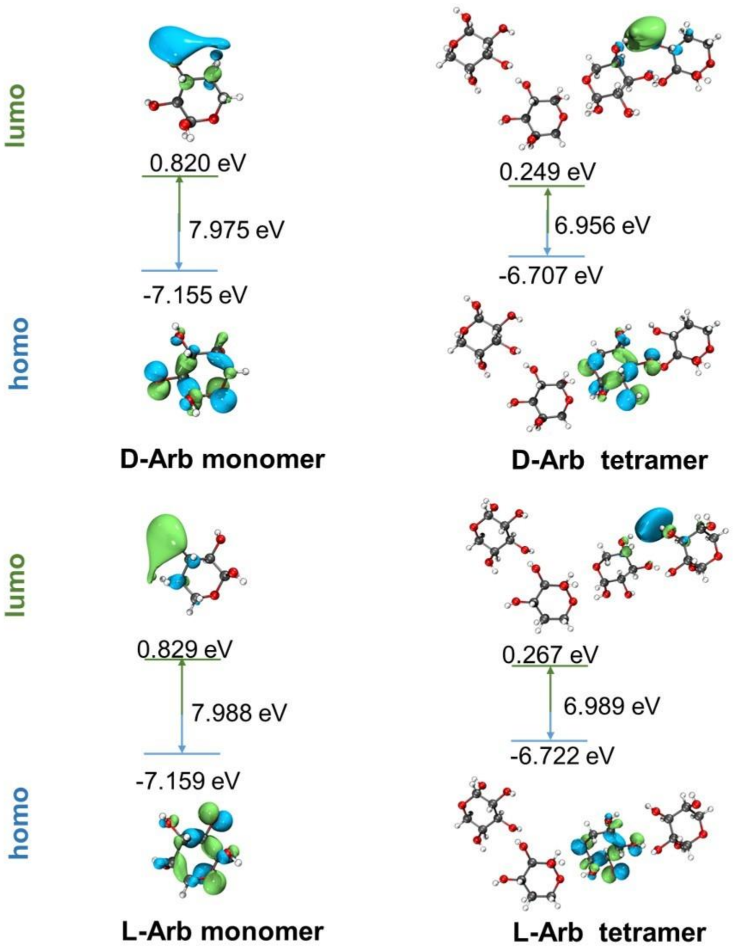

Fig. S6 Frontier molecular orbitals of D/L-Arb monomer, tetramer based on the ground-state geometries in the crystalline phase iso-value = 0.05

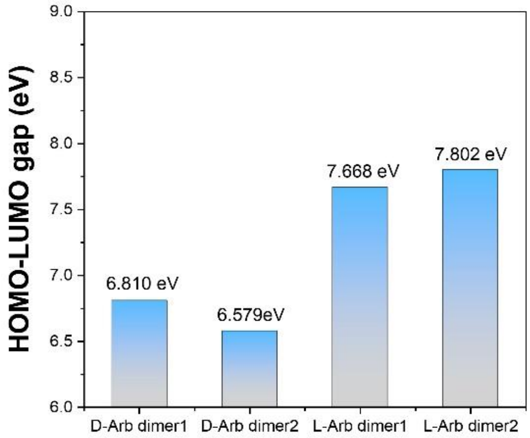

Fig. S7 HOMO-LUMO gap of D-Arb dimer1，D-Arb dimer2，L-Arb dimer1, L-Arb dimer2

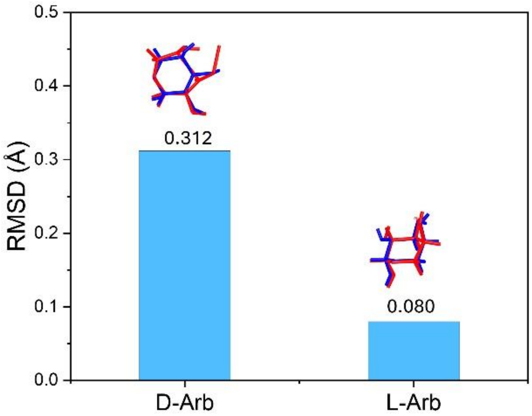

Fig. S8 The RMSD values of the atomic positions were calculated to evaluate the strength of intramolecular motion in two different states (ground-state (blue colour) and excited-state T1 (red colour) geometries of D/L-Arb molecule.

Name	**D-Arabinose**
CCDC	2399877
Empirical formula	$C_5H_{10}O_5$
Formula weight	150.13
Temperature/K	299.44(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	4.8396(3)
b/Å	6.5160(3)
c/Å	19.4563(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	613.55(6)
Z	4
ρ_{calc}g/cm^3	1.625
μ/mm^{-1}	0.147
F (000)	320.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.186 to 50.216
Index ranges	$-4 \le h \le 5$, $-7 \le k \le 6$, $-23 \le l \le 19$
Reflections collected	2748
Independent reflections	1091 [R_{int} = 0.0221, R_{sigma} = 0.0274]
Data/restraints/parameters	1091/0/95
Goodness-of-fit on F^2	1.074
Final R indexes [I>=2σ (I)]	R_1 = 0.0312, wR_2 = 0.0738
Final R indexes [all data]	R_1 = 0.0346, wR_2 = 0.0759
Largest diff. peak/hole / e Å^{-3}	0.13/-0.17
Flack parameter	-1.5(8)

Table. S1 Single crystal analysis report of D-Arb crystal data and structure refinement

CCDC2399877

Name	**L-Arabinose**
CCDC	2399878
Empirical formula	$C_5H_{10}O_5$
Formula weight	150.13
Temperature/K	299.50(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	4.8438(2)
b/Å	6.5220(4)
c/Å	19.4436(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	614.25(6)
Z	4
ρ_{calc}g/cm^3	1.623
μ/mm^{-1}	0.147
F (000)	320.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.19 to 50.184
Index ranges	$-5 \le h \le 5$, $-5 \le k \le 7$, $-22 \le l \le 23$
Reflections collected	2698
Independent reflections	1091 [R_{int} = 0.0254, R_{sigma} = 0.0344]
Data/restraints/parameters	1091/0/95
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0352, wR_2 = 0.0780
Final R indexes [all data]	R_1 = 0.0400, wR_2 = 0.0814
Largest diff. peak/hole / e Å^{-3}	0.15/-0.18
Flack parameter	-0.7(10)

Table. S2 Single crystal analysis report of L-Arb crystal data and structure refinement

CCDC2399878

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
🟥	2	x, y, z	4.84	B3LYP/6-31G (d, p)	-12.8	-3.9	-22.7	16.6	-25.9
🟨	2	x, y, z	6.52	B3LYP/6-31G (d, p)	-17.8	-5.3	-17.5	20.0	-25.7
🟩	2	-x, y+1/2, -z+1/2	6.40	B3LYP/6-31G (d, p)	-51.4	-9.7	-13.0	58.5	-36.7
🟦	2	-x, y+1/2, -z+1/2	5.95	B3LYP/6-31G (d, p)	-40.5	-11.6	-19.0	51.7	-36.1
🟦	2	x+1/2, -y+1/2, -z	6.17	B3LYP/6-31G (d, p)	-40.7	-8.5	-15.0	46.2	-33.9
🟪	2	x+1/2, -y+1/2, -z	6.94	B3LYP/6-31G (d, p)	-1.5	-1.2	-9.0	5.0	-7.1

Table. S3 D-Arb crystals use CE-B3LYP in CrystalExplorer to calculate the unit of energy for pomerwise interaction between molecules as kJ/mol, R= 3.22 Å

	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
🟥	2	x, y, z	4.84	B3LYP/6-31G (d, p)	-12.7	-3.8	-22.6	16.4	-25.8
🟨	2	x, y, z	6.52	B3LYP/6-31G (d, p)	-15.7	-4.9	-17.2	18.6	-23.7
🟩	2	x+1/2, -y+1/2, -z	6.94	B3LYP/6-31G (d, p)	-1.2	-1.2	-9.1	5.1	-6.9
🟦	2	-x, y+1/2, -z+1/2	5.95	B3LYP/6-31G (d, p)	-40.5	-11.5	-19.0	50.6	-36.6
🟦	2	x+1/2, -y+1/2, -z	6.17	B3LYP/6-31G (d, p)	-41.1	-8.5	-15.1	46.9	-34.0
🟪	2	-x, y+1/2, -z+1/2	6.41	B3LYP/6-31G (d, p)	-51.6	-9.7	-13.1	58.8	-36.9

Table. S4 L-Arb crystals use CE-B3LYP in CrystalExplorer to calculate the unit of energy for pomerwise interaction between molecules as kJ/mol, R= 3.22 Å

D-Arb	Excited state	Excitation energy (eV)	f	Transition configuration
monomer	S1	7.093	0.00358	H - 1 → L (85.5%), H → L (10.2%)
	S2	7.199	0.01228	H → L (85.3%), H - 1 → L (9.8%)
	S3	7.566	0.0221	H → L + 1 (58.1%), H → L + 2 (30.6%)
	S4	7.644	0.00547	H → L + 2 (52.8%), H → L + 1 (34.7%)
	S5	7.836	0.00885	H - 1 → L + 2 (38.1%), H - 1 → L + 3 (23.7%), H - 1 → L + 1 (17.5%), H - 3 → L (9.3%)
	T1	6.911		H - 1 → L (84.0%), H → L (5.9%)
	T2	7.116		H → L (81.6%), H - 1 → L (5.9%)
	T3	7.324		H → L + 2 (54.4%), H → L + 1 (18.1%), H → L (6.9%)
	T4	7.471		H → L + 1 (66.6%), H → L + 2 (15.2%)
	T5	7.579		H - 1 → L + 3 (33.9%), H - 1 → L + 2 (23.0%), H - 3 → L (13.5%), H - 1 → L + 1 (7.0%), H - 4 → L (5.3%)
tetramer	S1	6.254	0.01686	H-1 → L (50.0%), H → L (46.8%)
	S2	6.426	0.01284	H → L (51.1%), H-1 → L (46.0%)
	S3	6.839	0.00409	H-2 → L+1 (85.6%), H-2 → L (5.7%)
	S4	6.92	0.0007	H → L+1 (49.7%), H → L+3 (29.5%), H → L+2 (12.1%)
	S5	6.93	0.00069	H-2 → L (89.5%)
	T1	6.159		H-1 → L (52.3%), H → L (42.3%)
	T2	6.381		H → L (54.3%), H-1 → L (41.4%)
	T3	6.744		H-2 → L+1 (75.7%), H-5 → L+1 (6.2%)
	T4	6.788		H-8 → L (76.5%), H-6 → L (6.4%), H-7 → L (6.3%)
	T5	6.9		H → L+1 (37.8%), H → L+3 (30.6%), H → L+2 (12.3%), H-2 → L (5.9%)

Table. S5 Transition configurations of D-Arb monomer and tetramer.

L-Arb	Excited state	Excitation energy (eV)	f	Transition configuration
monomer	S1	7.113	0.00542	H-1 → L (68.2%), H → L (27.6%)
	S2	7.222	0.00918	H → L (67.5%), H-1 → L (26.7%)
	S3	7.56	0.02364	H → L+1 (57.1%), H → L+2 (32.3%)
	S4	7.644	0.00487	H → L+2 (52.9%), H → L+1 (34.8%)
	S5	7.875	0.00905	H-1 → L+2 (36.1%), H-1 → L+1 (23.8%), H-1 → L+3 (19.5%), H-3 → L (8.2%)
	T1	6.932		H-1 → L (75.4%), H → L (14.3%)
	T2	7.133		H → L (71.0%), H-1 → L (13.7%), H → L+1 (6.2%)
	T3	7.326		H → L+2 (52.0%), H → L+1 (19.8%), H → L (9.7%)
	T4	7.47		H → L+1 (62.8%), H → L+2 (17.2%)
	T5	7.618		H-1 → L+3 (37.0%), H-1 → L+2 (19.0%), H-3 → L (13.8%), H-4 → L (7.0%), H-1 → L+1 (6.8%)
tetramer	S1	6.3	0.01973	H → L (54.5%), H-1 → L (42.4%)
	S2	6.472	0.01043	H-1 → L (53.6%), H → L (43.4%)
	S3	6.856	0.00398	H-2 → L+1 (87.2%)
	S4	6.926	0.00069	H → L+1 (49.9%), H → L+3 (27.5%), H → L+2 (14.8%)
	S5	6.973	0.0017	H-8 → L (61.6%), H-7 → L (20.4%), H-2 → L (10.5%)
	T1	6.204		H → L (48.1%), H-1 → L (46.6%)
	T2	6.427		H → L (48.5%), H-1 → L (47.1%)
	T3	6.759		H-2 → L+1 (77.5%), H-5 → L+1 (6.1%)
	T4	6.818		H-8 → L (66.4%), H-7 → L (21.7%)
	T5	6.906		H → L+1 (41.8%), H → L+3 (31.4%), H → L+2 (17.1%)

Table. S6 Transition configurations of L-Arb monomer and tetramer.

References

1. F. Neese, Software update: The ORCA program system—Version 5.0, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2022, **12**, e1606.
2. T. Lu and F. Chen, Multiwfn: A multifunctional wavefunction analyzer, *J. Comput. Chem.*, 2012, **33**, 580-592.
3. T. Lu, A comprehensive electron wavefunction analysis toolbox for chemists, Multiwfn, *JCP*, 2024, **161**.
4. W. Humphrey, A. Dalke and K. Schulten, VMD: visual molecular dynamics, *J. Mol. Graphics*, 1996, **14**, 33-38.