Electronic Supplementary Information

Regulating the Excited State Chirality to Fabricate High-Performance-Solid-State Circularly Polarized Luminescence Materials

Jianlei Han^a, Yonghong Shi^{ab}, Xue Jin^a, Xuefeng Yang^{ab} and Pengfei Duan^{* ab}

- a. CAS Key Laboratory of Nanosystem and Hierarchical Fabrication, National Center for Nanoscience and Technology (NCNST), No. 11 ZhongGuanCun BeiYiTiao, Beijing 100190, P. R. China.
- b. University of Chinese Academy of Sciences, Beijing 100049, P. R. China

* Corresponding authors: Pengfei Duan E-mail: duanpf@nanoctr.cn

1.Experimental Procedures

1.1 Characterizations:

The ¹H NMR spectra were recorded on a Bruker Fourier300 spectrometer. Mass spectral data were obtained by using Autoflex tof/tofIII and HR Mass using a SolariX maldi-FTMS instrument. Thermal stability was evaluated through a Differential Scanning Calorimeter DSC822e and a thermogravimetric analyzer Perkin Elmer Diamond TG/DTA. FTIR studies were performed with Bruker Tensor-27 spectrometer. UV-vis spectra were recorded on Hitachi U-3900 spectrophotometer. Fluorescence spectra were obtained using F-4500 fluorescence spectrophotometer. Microscopy was recorded on the Olympus X83 using high-pressure mercury lamp as excitation source for fluorescent image (Movie 1 and Movie 2) or Leica DM2700M upright materials microscopes (Movie 3). POM images were recorded on Leica DM2700M upright materials microscope. CD and CPL spectra were measured on JASCO J-1500 and JASCO CPL-200 spectrophotometers, respectively. The absolute fluorescence quantum yield was measured by using an absolute PL quantum yield spectrometer (Edinburgh FLS-980 fluorescence spectrometer) with a calibrated integrating sphere and fluorescence lifetime measurements were recorded on Rigaku D/Max-2500 X-ray diffractometer (Japan) with Cu/K α radiation (λ =1.5406Å. The single-crystal X-ray diffraction data were collected using a X-ray diffractometer (XtaLAB Synergy-R, Rigaku, Japan).

1.2 Materials:

All reagents and solvents were used as received. 4-(*N*, *N*-dimethylamino) pyridinium-4-toluene sulfonate (DPTS) was prepared by mixing the solutions of dimethylaminopyridine (DMAP) and *p*-toluenesulfonic acid monohydrate in tetrahydrofuran (THF), after stirring for 30 min the precipitate was filtered and washed with THF and then dried in vacuum.

1.3 Synthesis:





R/S-1 have been reported by us¹, the same method was used for the other compounds. Here, take *R*-2 as an example. Dry dichloromethane (100 mL) was added into a round bottomed flask of 1-Pyrenecarboxylic Acid (0.54 g, 2.2 mmol), Binaphtol (0.29 g, 1 mmol) and DPTS (0.65 g, 2.2 mmol) under Ar, after stirred for 15 min, *N*, *N*²-diisopropylcarbodiimide (DIPC) (0.5 mL) was added into the reaction mixture at rt. Then the reaction mixture was stirred for 24h at rt. The reaction mixture was washed with water. The organic layer was separated and dried over Na₂SO₄. After evaporation of the solvent, the residue obtained was purified by column chromatography (petroleum ether/ ethyl acetate=100/1) to give the corresponding ester. IR v_{max}/cm^{-1} (KBr pellet): 3043, 1726, 1597, 1506, 1386, 1326, 1248, 1220, 1203, 1191, 1163, 1163, 1141, 1126, 1118, 1080, 1035, 1022, 974, 850, 831, 802, 744, 707. ¹H NMR (300 MHz, Chloroform-d) δ 8.86 (d, J = 9.3 Hz, 2H), 8.22 – 7.83 (m, 20H), 7.80 – 7.70 (m, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.45 (m, 4H). MS (Maldi) calcd for C₅₄H₃₀O₄+Na [M+Na]+:765.2, found: 765.2



*R-*3

IR v_{max}/cm^{-1} (KBr pellet): 3037, 2950, 2848, 1718, 1597, 1581, 1506, 1465, 1386, 1325, 1247, 1222, 1191, 1166, 1124, 1080, 1031, 848, 704¹H NMR (300 MHz, Chloroform-*d*) δ 9.33 (d, J = 9.5 Hz, 2H), 8.28 – 8.14 (m, 8H), 8.05 (d, J = 8.1 Hz, 4H), 7.88 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2 H), 7.24 – 7.19 (m, 2H), 6.99 (d, J = 7.1 Hz, 2H), 3.07 (dt, J = 17.9, 9.4 Hz, 2H), 2.91 (s, 2H), 2.46 – 2.34 (m, 4H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 165.58 , 147.62 , 146.15 , 140.09 , 134.56 , 131.82 , 130.89 , 130.28 , 129.79 , 129.57 , 128.87 , 128.00 , 127.14 , 126.34 , 126.29 , 126.23 , 124.85 , 123.99 , 122.32 , 121.63 , 121.60 , 59.34 , 38.50 , 31.23 . HRMS (Maldi) calcd for C₅₁H₃₂O₄+Na [M+Na]⁺:731.2198, found: 773.2189



IR v_{max}/cm^{-1} (KBr pellet): 3041, 2931, 1724, 1597, 1494, 1411, 1251, 1222, 1190, 1132, 1089, 1029, 896, 846, 711. ¹H NMR (300 MHz, Chloroform-*d*) δ 9.33 (d, *J* = 9.5 Hz, 2H), 8.92 (d, *J* = 8.1 Hz, 2H), 8.10 (d, *J* = 7.6 Hz, 2H), 8.07 - 7.94 (m, 8H), 7.95 - 7.83 (m, 4H), 7.02 (d, *J* = 1.7 Hz, 2H), 6.70 (d, *J* = 7.9 Hz, 2H), 6.54 (dd, *J* = 7.9, 9.102 (dz) = 1.7 Hz, 2H), 6.70 (dz) = 7.9 Hz, 2H), 6.54 (dz) = 7.9, 6.54 (dz) = 7.

1.8 Hz, 2H), 3.45 - 3.32 (m, 2H), 3.20 - 3.03 (m, 4H), 2.92 - 2.76 (m, 2H). MS (Maldi) calcd for $C_{50}H_{32}O_4$ +Na [M+Na]⁺:719.2, found: 719.3



Dry dichloromethane (100 mL) was added into a round bottomed flask of 1-Pyrenecarboxylic Acid (0.3 g, 1 mmol), Octahydrobinaphtol (0.29 g, 1 mmol) and DPTS (0.3 g, 1 mmol) under Ar, after stirred for 15 min, DIPC (0.1 mL) was added into the reaction mixture at rt. Then the reaction mixture was stirred for 24h at rt. The reaction mixture was washed with water. The organic layer was separated and dried over Na₂SO₄. After evaporation of the solvent, the residue obtained was purified by column chromatography (petroleum ether/ DCM=5/2) to give bipyrene and mono-pyrene compounds successively.

Mono-pyrene compound. IR v_{max} /cm⁻¹ (KBr pellet): 3465, 3043, 2927, 2850, 1720,1593, 1475, 1257, 1215, 1191, 1126, 1080, 1028, 848, 707. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.86 (d, *J* = 9.4 Hz, 1H), 8.32 – 8.23 (m, 3H), 8.18 (dd, *J* = 9.2, 6.5 Hz, 2H), 8.12 – 8.03 (m, 3H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.76 (d, *J* = 8.3 Hz, 1H), 2.92 m Hz, 2H), 2.73 (m, 2H), 2.66 – 2.44 (m, 2H), 2.41 – 2.13 (m, 2H), 1.92 – 1.67 (m, 8H).

5 mL DMF was added into a round bottomed flask containing mono-pyrene compound (0.26 g, 0.5 mmol), K₂CO₃ and 2 mL bromoethane. Then the mixture was heated to 50 °C for 4 h. After cooling to room temperture, 50 mL DCM was added into the reaction mixture. The organic layer was washed with water. The organic layer was separated and dried over Na₂SO₄. After evaporation of the solvent, the residue obtained was purified by column chromatography (petroleum ether/ ethyl acetate=20/1) to give **R-5**. IR v_{max}/cm^{-1} (KBr pellet):3043, 2976, 2929, 2856, 1722, 1657, 1593, 1539, 1510, 1471, 1249, 1211, 1190, 1163, 1126, 1082, 1028, 850, 796, 709. ¹H NMR (300 MHz, Chloroform-*d*) δ 8.86 (d, *J* = 9.4 Hz, 1H), 8.23 (dd, *J* = 7.6, 3.6 Hz, 2H), 8.18 – 7.96 (m, 6H), 7.30 – 7.19 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 3.91 (m, 2H), 2.89 (t, *J* = 6.2 Hz, 2H), 2.79 – 2.70 (m, 2H), 2.62 – 2.39 (m, 2H), 2.41 – 2.17 (m, 2H), 1.86 – 1.61 (m, 8H), 1.14 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (75 MHz, Chloroform-*d*) δ 154.05 , 146.38 , 137.41 , 137.02 , 134.70 , 134.17 , 130.95 , 130.39 , 130.21 , 129.64 , 129.52 , 129.24 , 129.10 , 128.68 , 128.48 , 127.10 , 126.22 , 126.14 , 126.10 , 125.22 , 124.87 , 123.92 , 119.66 , 110.04 , 63.86 , 29.73 , 29.42 , 27.40 , 27.30 , 23.27 , 23.23 , 23.11 , 23.03 , 14.75 . HRMS (Maldi) calcd for C₃₉H₃₄O₃+Na [M+Na]⁺:573.2406, found: 573.2401

2. Results and Discussion



Fig. S1 Normalized absorption spectra of *S*-1 solution, and solid diffuse reflectance spectra of pristine sample and microcrystals.



Fig. S2 Photograph of polymorphic phase transition from amorphous powder to crystal in ethyl acetate. a) i) ethyl acetate was added to *S*-1 powder, the transition from amorphous powder to crystal is very fast that as the picture shows. ii) the rest of yellow solid was covered by colorless solid. iii) after complete transition. b) emission picture after transition from amorphous powder under UV-365 nm irradiation.



Fig. S3 Optical microscopy images (a, c) and POM micrographs (b, d) of pristine sample (a, b) and microcrystals (c, d)



Fig. S4 Optical microscopy image (a) and fluorescence microscopy image (b) before and after (c) a drop of EA was added to induce the transfer, this process happened very quickly and the flowing EA carried sample to somewhere else, so that no profile of the initial state can be found.



Fig. S5 Optical microscopy images and fluorescence microscopy images of pristine (a, b), microcrystals precipitating from ethyl acetate (c, d) and crystal obtained from solvent evaporation the ethyl acetate/dichloromethane solution (e, f).



Fig. S6 Thermogravimetric analysis (TGA) of pristine and microcrystals and the curves show high thermal stability up to 420 °C.



Fig. S7 (a) Photographs of pristine before (left) and after (right) annealing treatment under day light (upper panel) and UV-365 light (lower panel). b) XRD pattern of pristine and annealed sample.



Fig. S8 Normalized PL spectra of different samples excited by 360 nm.



Fig. S9 (a) The molecular structure of *S*-1.



Fig. S10 Intermolecular interactions along the b axis, π - π interactions between pyrene rings were omitted for clearity.



Fig. S11 Intermolecular interactions in the ac plane.



Fig. S12 Normalized UV-Vis and PL of S-1 (1.0×10^{-5} M, $\lambda_{ex} = 360$ nm) in ethyl acetate.



Fig. S13 Fluorescence lifetimes of *S*-1 in ethyl acetate (1.0×10^{-5} M, $\lambda_{ex} = 344$ nm, $d_{etected} = 410$ nm) and *S*-1 microcrystal ($\lambda_{ex} = 344$ nm, $d_{etected} = 470$ nm).



Fig. S14 Photographs of S-1 microcrystals and the grinding process under day light and UV light (365 nm).



Fig. S15 Photographs of *S*-1 microcrystals in mortar with the grinding process under UV irradiation (365 nm).



Fig. S16 Powder XRD patterns of different samples.



Fig. S17 Intermolecular interactions (a) and molecular packing structure (b) of *S*-2 (Hydrogen atoms were omitted for clarity).



Fig. S18 (a) molecular structure of **2**. (b) PL spectra of **2** in different states, insert shows emission photograph of **2** in ground and fumed states under UV 365 light. (c) PXRD patterns of **2** in ground, fumed states and simulated one from *S*-**2**.



Fig. S19 (a) molecular structure of 2. (b) PL spectra of **3** in different states, insert shows emission photograph of **3** in pristine, ground and fumed states under UV 365 light. (c) The corresponding PXRD patterns and the simulated XRD from *R*-**3**.



Fig. S20 Molecular packing structure of *R*-3 (Hydrogen atoms were omitted for clarity).



Fig. S21 (a) molecular structure of 4. (b) Photographs of 4 in a mortar after ground and fumed, it can be seen the samples in the red ring show no emission, while scratched part in blue frame emits green light. the emission of crystals was so weak that emission QY can't be detected. (c) PL spectra of 4 in different states, insert shows emission photograph of 4 in crystalline, ground and fumed states under UV 365 light. d) The corresponding PXRD patterns and the simulated XRD from R-4.



Fig. S22 Molecular packing structure of *R*-4 (Hydrogen atoms were omitted for clarity).

	QY ^[a] /%			$ au^{[b]}/ns$		
	ground	fumed	powder	ground	fumed	
<i>R</i> -1	55.8	49.8	29.5	31.1	33.4	
<i>R</i> -2	59.9	58.6	27.6	29.6	30.7	
<i>R</i> -3	3.1	-	31.6	28.3	13.5	
<i>R</i> -4	47.5	44.8	36.2	28.4	41.8	
<i>R</i> -5	53.3	51.3	31.2	31.7	21.2	

Table S1. Photophysical data of R-1- R-5

^[a] fluorescence quantum yield; ^[b] fluorescence lifetime excited by 365 nm.

	Centroid-centroid distances(Å)	Centroid-plane distance (Å)	Angle of two plane (0)	Overlapped area (%)
<i>S</i> -1	3.704	3.404	3.59	49.5
<i>S</i> -2	3.792	3.338	4.65	49.6
<i>R</i> -3	3.594	3.420	2.46	61.3
<i>R</i> -4	3.820	3.452	1.79	61.3
<i>R</i> -5	3.898	3.376	1.53	49.4

Table S2. π - π distance and the π - π overlapped of 1- 5 crystals



Fig. S23 CPL spectra of *R*/*S*-1 pristine ($\lambda_{ex} = 360$ nm).



Fig. S24 CD (a) and CPL (b) spectra of R/S-1 pristine. ($\lambda_{ex} = 360$ nm).



Fig. S25 SEM image of *R*-1 after the ground sample was fumed with ethyl acetate.



Fig. S26 CPL spectra of *R*-1 funed sample with front side excitation, front side rotating with 90° and 45°, and back side excitation ($\lambda_{ex} = 360$ nm).



Fig. S27 CPL spectra of *R*-2/*S*-2 pristine samples ($\lambda_{ex} = 360$ nm).



Fig. S28 CPL spectra of *R*-2/*S*-2 fumed samples ($\lambda_{ex} = 360$ nm).



Fig. S29 CPL spectra of *R*-3/*S*-3 pristine samples ($\lambda_{ex} = 360$ nm).



Fig. S30 CPL spectra of *R*-3/*S*-3 fumed samples ($\lambda_{ex} = 360$ nm).



Fig. S31 g_{CD} spectra of *R/S*-4 in different states.

Table S3 CD and CPL signs in different states								
	Film	Aggreg	ate ^[a]	Pristine	Fu	med	Solut	tion ^[b]
		Static excimer 2			Static e	xcimer 1	Dynamie	e excimer
	CPL	CD	CPL	CPL	CD	CPL	CD	CPL
R1	_	_	_	_	+	+	_	+
S 1	+	+	+	+	_	<u> </u>	+	-
R2	_	_	_	_	+	+	_	+
S2	+	+	+	+	-	_	+	_
R3	_	_	_	-	+	+	_	nd
S3	+	+	+	+	-	_	+	nd
R4	_	—	_	_	+	nd	_	_
S4	+	+	+	+	_	nd	+	+

^[a] The aggregate states were obtained by injecting 4 mL water into 0.5 mL 1.0×10^{-3} M THF solution. ^[b] in THF with the concentration of 1.0×10^{-2} M.



Fig. S32 (a) CD spectra of *R*-1/*S*-1 solution (THF, 2.5×10^{-3} M, 1 mm cell). (b) CPL spectra of *R*1/*S*1 solution (THF, 1.0×10^{-2} M, 1 mm cell) ($\lambda_{ex} = 360$ nm).



Fig. S33 CD and CPL spectra of *R*-1/*S*-1 film (a, b) and aggregates (c, d) (The aggregate states were obtained by injecting 4 mL water into 0.5 mL 1.0×10^{-3} M THF solution, $\lambda_{ex} = 360$ nm).



Fig. S34 Normalized Uv-vis spectra of *R*-1 (solution: THF, 1.1×10^{-4} M, aggregate: The aggregate states were obtained by injecting 4 mL water into 0.5 mL 1.0×10^{-3} M THF solution.). (b) Normalized PL spectra of *R*-1 (solution: THF, 1.1×10^{-4} M, aggregate: The aggregate states were obtained by injecting 4 mL water into 0.5 mL 1.0×10^{-3} M THF solution, $\lambda_{ex} = 360$ nm).



Fig. S35 PL spectra of *R*-1 (a), *R*-2 (a), *R*-3 (a), and *R*-4 (a) (solution: THF, 1.0×10^{-2} M, aggregate: the aggregate states were obtained by injecting 4 mL water into 0.5 mL 1.0×10^{-3} M THF solution.) ($\lambda_{ex} = 360$ nm).



Fig. S36 CD and CPL spectra of *R*-2/*S*-2 solution (a, b) (conditions for CD spectra: THF, 2.5×10^{-4} M, 1 mm cell, conditions for CPL spectra: THF, 1.0×10^{-2} M and aggregates) and aggregates (c, d) (The aggregate states were obtained by injecting 4 mL water into 0.5 mL 1.0×10^{-3} M THF solution.) ($\lambda_{ex} = 360$ nm).



Fig. S37 CD and CPL spectra of *R*-3/*S*-3 solution (a, b) (conditions for CD spectra: THF, 2.5×10^{-4} M, 1 mm cell, conditions for CPL spectra: THF, 1.0×10^{-2} M and aggregates) and aggregates (c, d) (The aggregate states were obtained by injecting 4 mL water into 0.5 mL 1.0×10^{-3} M THF solution.) ($\lambda_{ex} = 360$ nm).



Fig. S38 CD and CPL spectra of *R*-4/*S*-4 solution (a, b) (conditions for CD spectra: THF, 2.5×10^{-4} M, 1 mm cell, conditions for CPL spectra: THF, 1.0×10^{-2} M and aggregates) and aggregates (c, d) (The aggregate states were obtained by injecting 4 mL water into 0.5 mL 1.0×10^{-3} M THF solution.) ($\lambda_{ex} = 360$ nm).



Fig. S39 (a) molecular structure of 5. (b) PL spectra of 5 in different states, insert shows emission photograph of 5 in pristine, ground and fumed states under UV 365 light. (c) The corresponding PXRD patterns.



Fig. S40 CPL spectra of *R*-5/*S*-5 in different states (solution: THF, 1.0×10^{-2} M, aggregate: the aggregate states were obtained by injecting 4 mL water into 0.5 mL 1.0×10^{-3} M THF solution.) ($\lambda_{ex} = 360$ nm).



Fig. S41 (a) Structures of *cisoid* and *transoid* conformations of the binaphthyl derivatives with (R)-configuration. M-helicity corresponds a *cisoid* conformation ($0^{\circ} < \theta < 90^{\circ}$), P-helicity corresponds a *transoid* conformation ($90^{\circ} < \theta < 180^{\circ}$)². (b)The dihedral angle (θ) between the two ctahydrobinaphthyl rings of *R***-5** in the crystal.



Fig. S42 Molecular packing structure of *R*-5 in the crystal.

CCDC NO.	2104398
Empirical formula	C ₅₄ H ₃₈ O ₄
Formula weight	750.84
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	P 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	$a = 25.8331(11) \text{ Å}$ $a = 90^{\circ}.$
b = 10.6809(5) Å	b=90°.
c = 13.7334(5) Å	$g = 90^{\circ}$.
Volume	3789.3(3) Å ³
Z	4
Theta range for data collection	1.679 to 24.995°.
Index ranges	-30<=h<=30, -12<=k<=12, -16<=l<=16

Table S5. Crystallographic and structural refinement data of S-2 and R-3				
CCDC NO.	2104395	2104396		
Identification code	S- 2	R- 3		
Empirical formula	$C_{54}H_{30}O_4$	$C_{51}H_{32}O_4$		
Formula weight	742.78	740.81		
Temperature/K	170.00(10)	169.99(16)		
Crystal system	orthorhombic	orthorhombic		
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁		
a/Å	10.2762(4)	7.2123(2)		
b/Å	13.1669(5)	17.9092(4)		
c/Å	26.8750(9)	27.4926(5)		
α/°	90	90		
β/°	90	90		
γ/°	90	90		
Volume/Å ³	3636.3(2)	3551.12(14)		
Z	4	4		
2Θ range for data collection/°	3.444 to 60.902	5.89 to 150.852		
Index ranges	$\begin{array}{l} \text{-14} \leq h \leq 14, \text{-18} \leq k \leq 17, \\ \text{-38} \leq l \leq 37 \end{array}$	$-9 \le h \le 8, -22 \le k$ $\le 22,$ $-34 \le 1 \le 29$		

Table S6. Crystallographic and structural refinement data of R-4 and R-5				
CCDC NO.	2104394	2104397		
Identification code	<i>R</i> -4	<i>R</i> -5		
Empirical formula	$C_{50}H_{32}O_4$	$C_{39}H_{34}O_3$		
Formula weight	696.75	550.66		
Temperature/K	169.97(11)	169.99(12)		
Crystal system	monoclinic	monoclinic		
Space group	P2 ₁	P2 ₁		
a/Å	6.95280(10)	10.96470(10)		
b/Å	13.30690(10)	18.78190(10)		
c/Å	37.0562(4)	14.28420(10)		
α/°	90	90		
β/°	91.9510(10)	98.4040(10)		
$\gamma/^{\circ}$	90	90		
Volume/Å ³	3426.46(7)	2910.07(4)		
Z	4	4		
2Θ range for data collection/°	4.772 to 150.43	6.254 to 150.476		
Index ranges	$\begin{array}{l} -8 \leq h \leq 8, \text{-}15 \leq k \leq 16, \\ -45 \leq l \leq 45 \end{array}$	$-13 \le h \le 13, -23 \le k \le 23, -17 \le l \le 17$		

3. Reference

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- 2 H. Hayasaka, T. Miyashita, M. Nakayama, K. Kuwada and K. Akagi, J. Am. Chem. Soc., 2012, 134, 3758-3765.