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Selective molecular tailoring for retarders with achromaticity or a wide field-of-view

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1. Synthesis conditions of HRM molecules

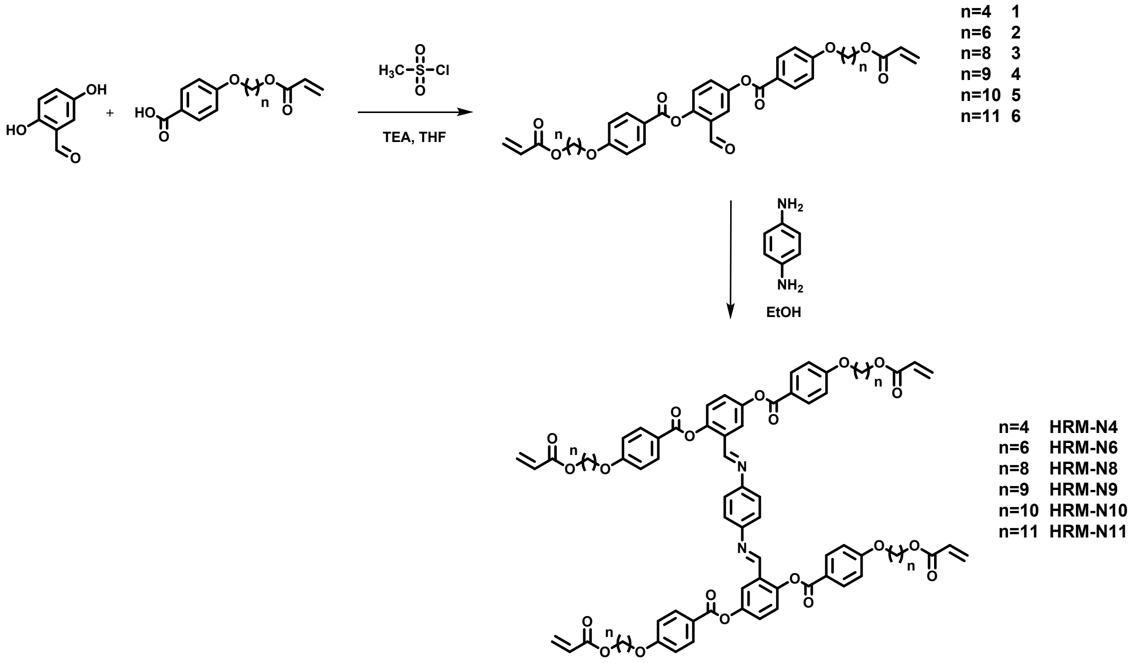


Fig. S1. Synthetic scheme of HRM molecules by alkyl chain length

2-formyl-1,4-phenylene bis(4-(4-(acryloyloxy)butoxy)benzoate) (1)

To a solution of 4-((4-(acryloyloxy)butyl)oxy)benzoic acid (8.42 g, 31.86 mmol) in THF (25 mL) was added triethylamine (14.13 mL, 101.36 mmol), and methanesulfonyl chloride (3.36 mL, 43.44 mmol) at 0 °C. The reaction mixture was stirred for 3h under nitrogen atmosphere. To the reaction mixture was added to 2,5-dihydroxybenzaldehyde (2.0 g, 14.48 mmol) in THF (10 mL). The reaction mixture was further stirred for 18 h at 60 °C. The reaction was quenched by water and the mixture was extracted with ethyl acetate. The organic solvent was removed under reduced pressure and the residue was purified by washing with ethanol to give a white solid (5.5 g, 60%). ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.21 (s, 1H), 8.19 – 8.14 (m, 4H), 7.79 (d, J = 2.9 Hz, 1H), 7.54 (dd, J = 8.8, 2.9 Hz, 1H), 7.39 (d, J = 8.8 Hz, 1H), 7.01 – 6.98 (m, 4H), 6.44 – 6.40 (m, 2H), 6.16 – 6.10 (m, 2H), 5.84 (dt, J = 10.4, 1.1 Hz, 2H), 4.27 (t, J = 5.9 Hz, 4H), 4.13 – 4.09 (m, 4H), 1.95 – 1.89 (m, 8H); UV-Vis (CH$_2$Cl$_2$, nm) 269 nm.

HRM-N4

To a solution of compound **1** (0.5 g, 0.79 mmol) in ethanol (20 mL) was added *p*-phenylenediamine

(43 mg, 0.40 mmol). The reaction mixture was stirred for 5 h at 60 °C. After that, the reaction mixture was cooled to room temperature, and the resulting solid was filtered. The crude mixture was washed with ethanol to give a yellow solid (0.35 g, 66%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.60 (s, 2H), 8.18 – 8.15 (m, 8H), 8.05 (d, *J* = 2.8 Hz, 2H), 7.39 (dd, *J* = 8.8, 2.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 2H), 7.13 (s, 4H), 7.03 – 6.99 (m, 8H), 6.38 (ddd, *J* = 17.4, 4.6, 1.5 Hz, 4H), 6.13 (ddd, *J* = 17.4, 10.5, 4.7 Hz, 4H), 5.82 (ddd, *J* = 10.4, 6.3, 1.5 Hz, 4H), 4.23 (td, *J* = 6.1, 4.1 Hz, 8H), 4.11 (q, *J* = 5.8 Hz, 8H), 1.91 (m, 16H); FAB-MS m/z: calcd for $C_{76}H_{72}N_2O_{20}$ 1332.47, found: 1333 $[M+H]^+$; UV-Vis (CH_2Cl_2, nm) 268 nm, 364 nm.

2-formyl-1,4-phenylene bis[4-(6-acryloyloxyhexyloxy)]benzoate (2)

To a solution of 4-(6-acryloyloxyhexyloxy)benzoic acid (9.35 g, 31.86 mmol) in THF (60 mL) was added to triethylamine (14.1 mL, 101.36 mmol) and methanesulfonyl chloride (3.4 mL, 43.44 mmol) at 0 °C. The reaction mixture was stirred for 3h. To the reaction mixture was added to 2,5 dihydroxybenzaldehyde (2.00 g, 14.48 mmol) in THF (10 mL) The reaction mixture was further stirred for 18 h at 65 °C. The reaction was quenched by water and the mixture was extracted with ethyl acetate. The organic solvent was removed under reduced pressure and the residue was purified by washing with ethanol to give a white solid (7.1 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.16 (dd, *J* = 12.3, 8.9 Hz, 4H), 7.79 (d, *J* = 2.8 Hz, 1H), 7.54 (dd, *J* = 8.8, 2.9 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 6.99 (d, 4H), 6.41 (dd, *J* = 17.3, 1.3 Hz, 2H), 6.13 (dd, *J* = 17.3, 10.4 Hz, 2H), 5.83 (dd, *J* = 10.4, 1.2 Hz, 2H), 4.19 (t, *J* = 6.6 Hz, 4H), 4.07 (td, *J* = 6.3, 3.6 Hz, 4H), 1.86 (m, 4H), 1.77 – 1.71 (m, 4H), 1.60 – 1.45 (m, 8H); UV-Vis (CH_2Cl_2, nm) 269 nm.

HRM-N6

To a solution of compound **2** (0.5 g, 0.73 mmol) in ethanol (15 mL) was added p-phenylenediamine (39 mg, 0.36 mmol). The reaction mixture was stirred for 6 h at 60oC. After that, the reaction mixture was cooled to room temperature, and the resulting solid was filtered. The crude mixture was washed with ethanol to give a yellow solid (0.47 g, 89%). ^{1}H NMR (400 MHz, Methylene Chloride-d$_2$) δ 8.60 (s, 2H), 8.16 (dd, *J* = 8.9, 2.1 Hz, 8H), 8.05 (d, *J* = 2.8 Hz, 2H), 7.39 (dd, *J* = 8.8, 2.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.00 (dd, *J* = 8.9, 2.4 Hz, 8H), 6.39 – 6.33 (m, 4H), 6.12 (ddd, *J* = 17.3, 10.4, 3.6 Hz, 4H), 5.82 – 5.78 (m, 4H), 4.16 (dt, *J* = 6.7, 3.4 Hz, 8H), 4.07 (d, *J* = 4.7 Hz, 8H), 1.84 (s, 8H), 1.74 – 1.69 (m, 8H), 1.57 – 1.45 (m, 16H); FAB-MS m/z: calcd for $C_{84}H_{88}N_2O_{20}$ 1444.59, found: 1446 [M+H]+ ; UV-Vis (CH_2Cl_2, nm) 269 nm, 365 nm.

2-formyl-1,4-phenylene bis(4-((8-(acryloyloxy)octyl)oxy)benzoate) (3)

To a solution of 4-((8-(acryloyloxy)octyl)oxy)benzoic acid (0.86 g, 2.68 mmol) in THF (20 mL) was added triethylamine (1.19 mL, 8.54 mmol), and methanesulfonyl chloride (0.28 mL, 3.66 mmol) at 0 °C. The reaction mixture was stirred for 2 h under a nitrogen atmosphere. To the reaction mixture was added to 2,5-dihydroxybenzaldehyde (0.17 g, 1.22 mmol) in THF (10 mL). The reaction mixture was further stirred for 6 h at 60 °C. The reaction was quenched by water and the mixture was extracted with ethyl acetate. The organic solvent was removed under reduced pressure and the residue was purified by washing with ethanol to give the white solid (0.62 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.21 (s, 1H), 8.16 (dd, *J* = 12.3, 8.6 Hz, 4H), 7.79 (d, *J* = 2.8 Hz, 1H), 7.53 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 6.99 (t, *J* = 8.1 Hz, 4H), 6.40 (dd, *J* = 17.3, 1.9 Hz, 2H), 6.13 (dd, *J* = 17.3, 10.4 Hz, 2H), 5.82 (dd, *J* = 10.4, 1.8 Hz, 2H), 4.16 (t, *J* = 6.8 Hz, 4H), 4.08 – 4.01 (m, 4H), 1.82 (q, *J* = 7.4 Hz, 4H), 1.68 (q, *J* = 6.9 Hz, 4H), 1.56 – 1.44 (m, 8H), 1.41 – 1.37 (m, 8H); UV-Vis (CH_2Cl_2, nm) 269 nm.

HRM-N8

To a solution of compound **3** (0.50 g, 0.67 mmol) in ethanol (20 mL) was added *p*-phenylenediamine (44 mg, 0.40 mmol). The reaction mixture was stirred for 6 h at 60 °C. After that, the reaction mixture was cooled to room temperature, and the resulting solid was filtered. The crude mixture was washed with ethanol to give a yellow solid (0.30 g, 57%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.60 (s, 2H), 8.15 (dd, *J* = 8.8, 2.4 Hz, 8H), 8.05 (d, *J* = 2.8 Hz, 2H), 7.39 (dd, *J* = 8.8, 2.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.12 (s, 4H), 7.00 (dd, *J* = 9.0, 2.6 Hz, 8H), 6.35 (ddd, *J* = 17.3, 3.1, 1.6 Hz, 4H), 6.11 (ddd, *J* =

17.3, 10.4, 3.2 Hz, 4H), 5.80 (ddd, *J* = 10.4, 3.6, 1.8 Hz, 4H), 4.13 (td, *J* = 6.7, 3.1 Hz, 8H), 4.06 (q, *J* = 5.9 Hz, 8H), 1.82 (t, *J* = 8.0 Hz, 8H), 1.67 (m, 8H), 1.52 – 1.36 (m, 32H); FAB-MS m/z: calcd for $C_{92}H_{104}N_2O_{20}$ 1556.72, found: 1558 $[M+H]^+$; UV-Vis (CH_2Cl_2, nm) 269 nm, 365 nm.

2-formyl-1,4-phenylene bis(4-((9-(acryloyloxy)nonyl)oxy)benzoate) (4)

To a solution of 4-((9-(acryloyloxy)nonyl)oxy)benzoic acid (2.0 g, 5.98 mmol) in THF (20 mL) was added triethylamine (2.65 mL, 19.03 mmol), and methanesulfonyl chloride (0.63 mL, 8.15 mmol) at 0 °C. The reaction mixture was stirred for 3 h under a nitrogen atmosphere. To the reaction mixture was added to 2,5-dihydroxybenzaldehyde (0.38 g, 2.72 mmol) in THF (10 mL). The reaction mixture was further stirred for 12 h at 25 °C. The reaction was quenched by water and the mixture was extracted with ethyl acetate. The organic solvent was removed under reduced pressure and the residue was purified by washing with ethanol to give the white solid (0.46 g, 80%). ^1H NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.16 (dd, *J* = 12.3, 8.6 Hz, 4H), 7.79 (d, *J* = 2.8 Hz, 1H), 7.53 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 6.99 (t, *J* = 8.1 Hz, 4H), 6.40 (dd, *J* = 17.3, 1.9 Hz, 2H), 6.13 (dd, *J* = 17.3, 10.4 Hz, 2H), 5.81 (dd, *J* = 10.4, 1.8 Hz, 2H), 4.16 (t, *J* = 6.8 Hz, 4H), 4.06 (m, 4H), 1.83 (m, 4H), 1.68 (m, 4H), 1.56 – 1.44 (m, 4H), 1.36 (m, 16H); UV-Vis (CH_2Cl_2, nm) 269 nm.

HRM-N9

To a solution of compound **4** (0.50 g, 0.65 mmol) in ethanol (20 mL) was added *p*-phenylenediamine (42 mg, 0.39 mmol). The reaction mixture was stirred for 6 h at 60 °C. After that, the reaction mixture was cooled to room temperature, and the resulting solid was filtered. The crude mixture was washed with ethanol to give a yellow solid (0.21 g, 40%). ^1H NMR (400 MHz, CD_2Cl_2) δ 8.61 (s, 2H), 8.16 (dd, *J* = 8.8, 2.4 Hz, 8H), 8.05 (d, *J* = 2.8 Hz, 2H), 7.39 (dd, *J* = 8.8, 2.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.13 (s, 4H), 7.00 (dd, *J* = 9.0, 2.6 Hz, 8H), 6.35 (ddd, *J* = 17.3, 3.1, 1.6 Hz, 4H), 6.11 (ddd, *J* = 17.3, 10.4, 3.2 Hz, 4H), 5.80 (ddd, *J* = 10.4, 3.6, 1.8 Hz, 4H), 4.13 (m, 8H), 4.06 (m, 8H), 1.82 (m, 8H), 1.67 (m, 8H), 1.48 – 1.36 (m, 40H); FAB-MS m/z: calcd for $C_{96}H_{112}N_2O_{20}$ 1612.78, found: 1613

$[M+H]^+$; UV-Vis (CH_2Cl_2, nm) 269 nm, 365 nm.

2-formyl-1,4-phenylene bis(4-((10-(acryloyloxy)decyl)oxy)benzoate) (5)

To a solution of 4-((10-(acryloyloxy)decyl)oxy)benzoic acid (0.55 g, 1.59 mmol) in THF (20 mL) was added triethylamine (0.7 mL, 5.07 mmol), and methanesulfonyl chloride (0.17 mL, 2.17 mmol) at 0 °C. The reaction mixture was stirred for 3 h under a nitrogen atmosphere. To the reaction mixture was added to 2,5-dihydroxybenzaldehyde (0.10 g, 0.72 mmol) in THF (5 mL). The reaction mixture was further stirred for 18 h at 60 °C. The reaction was quenched by water and the mixture was extracted with ethyl acetate. The organic solvent was removed under reduced pressure and the residue was purified by washing with ethanol to give the white solid (0.45 g, 78%). ^1H NMR (400 MHz, $CDCl_3$) δ 10.24 (s, 1H), 8.18 (dd, *J* = 12.4, 8.5 Hz, 4H), 7.81 (d, *J* = 2.8 Hz, 1H), 7.56 (dd, *J* = 9.0, 2.8 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 1H), 7.02 (t, *J* = 8.1 Hz, 4H), 6.43 (d, *J* = 17.4 Hz, 2H), 6.15 (dd, *J* = 17.3, 10.4 Hz, 2H), 5.84 (d, *J* = 10.4 Hz, 2H), 4.18 (t, *J* = 6.8 Hz, 4H), 4.12 – 4.01 (m, 4H), 1.89 – 1.82 (m, 4H), 1.74 – 1.65 (m, 4H), 1.51 (t, *J* = 7.6 Hz, 4H), 1.43 – 1.30 (m, 20H); UV-Vis (CH_2Cl_2, nm) 269 nm.

HRM-N10

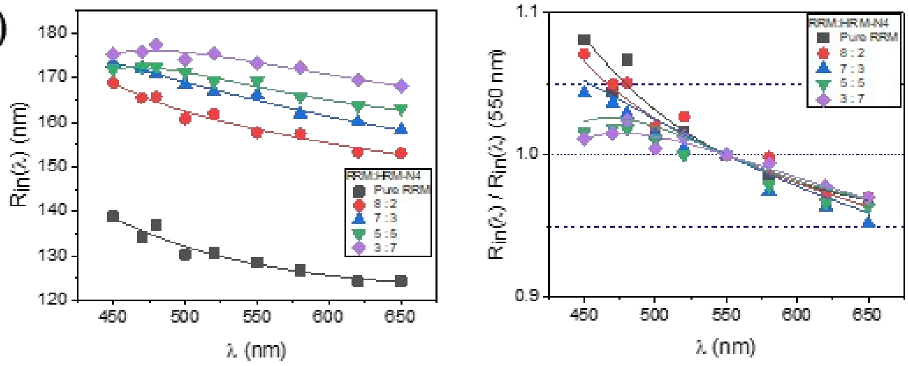
To a solution of compound **5** (0.2 g, 0.25 mmol) in ethanol (15 mL) was added *p*-phenylenediamine (16 mg, 0.15 mmol). The reaction mixture was stirred for 5 h at 60 °C. After that, the reaction mixture was cooled to room temperature, and the resulting solid was filtered. The crude mixture was washed with ethanol to give a yellow solid (0.15 g, 72%). ^1H NMR (500 MHz, CD_2Cl_2) δ 8.60 (s, 2H), 8.17 – 8.13 (m, 8H), 8.05 (d, *J* = 2.9 Hz, 2H), 7.39 (dd, *J* = 8.8, 2.9 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 2.5 Hz, 4H), 7.02 – 6.98 (m, 8H), 6.35 (ddd, *J* = 17.4, 3.2, 1.6 Hz, 4H), 6.11 (ddd, *J* = 17.3, 10.4, 3.5 Hz, 4H), 5.80 (ddd, *J* = 10.4, 3.7, 1.6 Hz, 4H), 4.12 (td, *J* = 6.7, 3.9 Hz, 8H), 4.06 (q, *J* = 6.4 Hz, 8H), 1.82 (ddt, *J* = 10.1, 6.5, 3.3 Hz, 8H), 1.69 – 1.62 (m, 8H), 1.50 – 1.44 (m, 8H), 1.39 – 1.30 (m, 40H); FAB-MS m/z: calcd for $C_{100}H_{120}N_2O_{20}$ 1668.84, found: 1670 $[M+H]^+$; UV-Vis (CH_2Cl_2, nm) 269 nm, 365 nm.

2. Retardation and optical property of the retarders and the HRM molecules

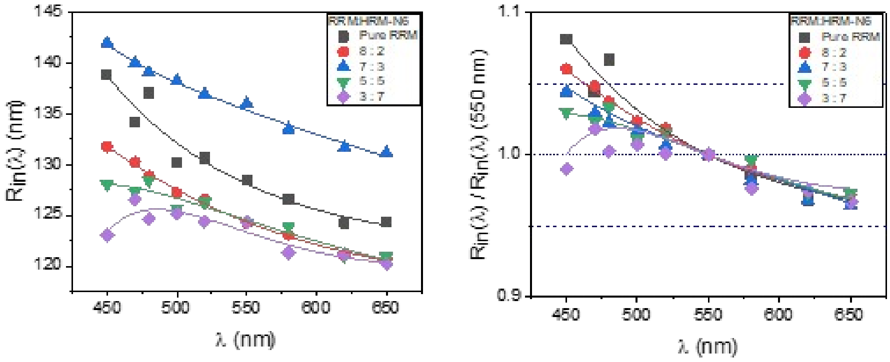
Table S1. Birefringence of the retarders made from pure RRM and RRM-HRM mixtures.

Alkyl chain length	Name	Thickness (μm)	Δn
-	RRM	1.03	0.125
4	HRM-N4	1.04	0.163
6	HRM-N6	1.05	0.118
8	HRM-N8	1.07	0.103
9	HRM-N9	1.05	0.115
10	HRM-N10	1.06	0.127
11	HRM-N11	1.05	0.093

(a)



(b)



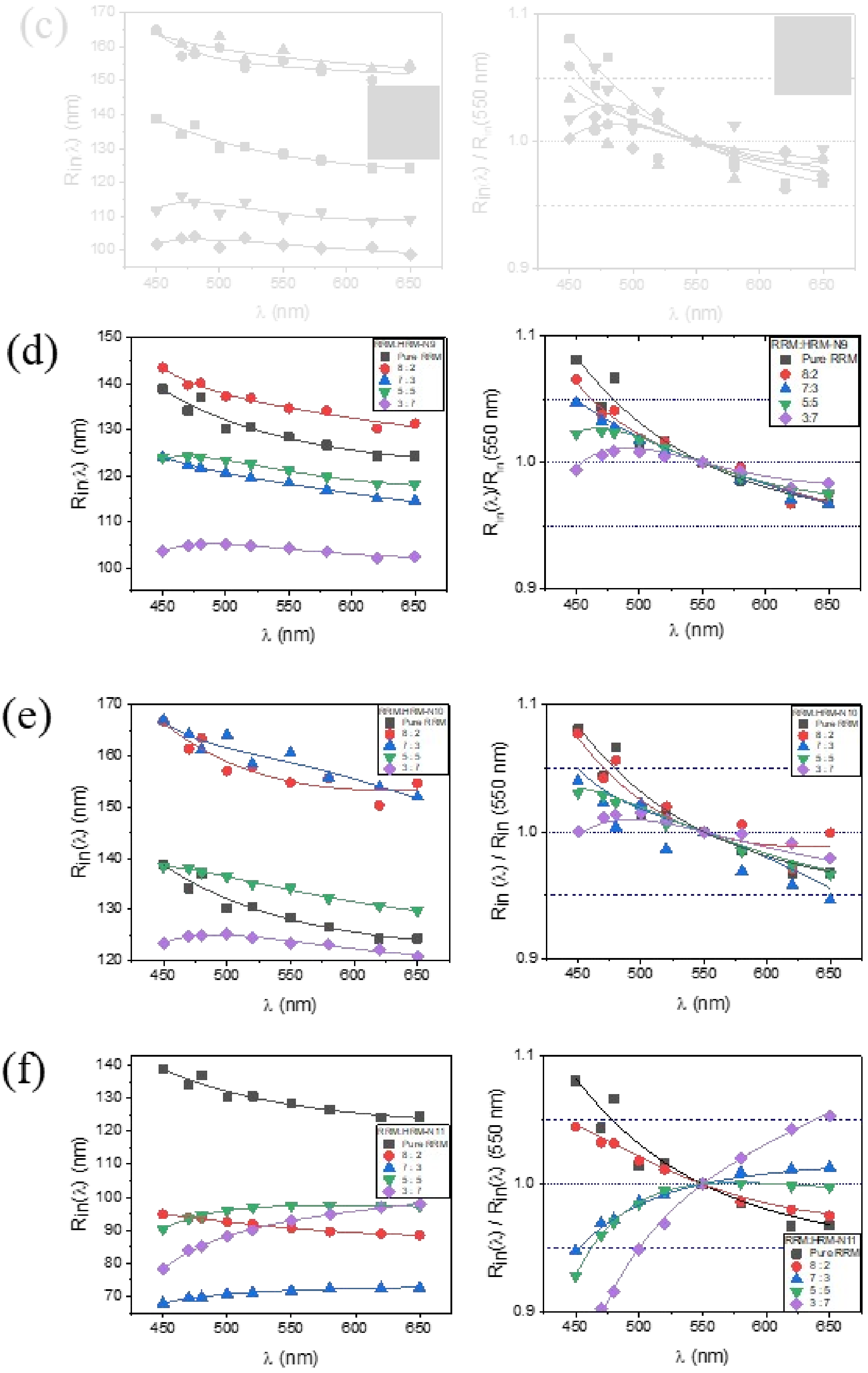


Fig. S2. In-plane retardation $R_{in}(\lambda)$ and normalized retardation $R_{in}(\lambda)/R_{in}(550\ nm)$ of the retarder made from pure RRM and RRM-HRM mixtures. HRM molecules of (a) N=4, (b) N=6, (c) N=8, (d) N=9 (e) N=10, and (f) N=11 were mixed with RRM.

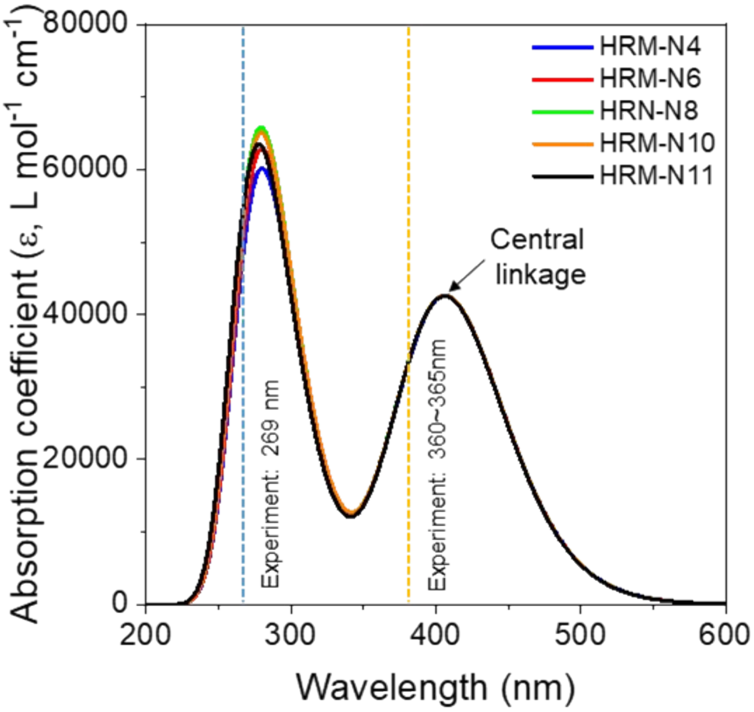


Fig. S3. Theoretically calculated UV-Vis absorption coefficient of the HRM molecules for comparing experimental data.

Table S2. The percentage errors (%) between calculated and experimental values of UV-Vis. absorption intensity.

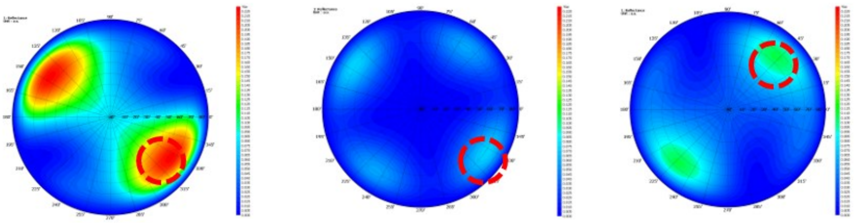
Alkyl chain length	Name	Calculation data		Experiment data		Error (%)	
		1st peak	2nd peak	1st peak	2nd peak	1st peak	2nd peak
4	**HRM-N4**	**279.6**	**405.6**	269	360	3.94	12.67
6	**HRM-N6**	**279.6**	**405.6**	269	365	3.94	11.12
8	**HRM-N8**	**279.6**	**405.6**	269	365	3.94	11.12
10	**HRM-N10**	**279.6**	**405.6**	269	365	3.94	11.12
11	**HRM-N11**	**277.2**	**405.6**	269	364	3.05	11.43

3. Detailed simulation results of application demonstration

Table S3. Simulation parameters of each layer which were used for the optical simulations.

Material	n_x-n_y			n_x-n_z			n_y-n_z			**Thickness (μm)**
	$\lambda = 450\ nm$	$\lambda = 550\ nm$	$\lambda = 650\ nm$	$\lambda = 450\ nm$	$\lambda = 550\ nm$	$\lambda = 650\ nm$	$\lambda = 450\ nm$	$\lambda = 550\ nm$	$\lambda = 650\ nm$	
RRM	0.135	0.125	0.119	0.144	0.134	0.127	0.009	0.009	0.008	**1.1**
WRS	0.003	0.003	0.003	0.003	0.003	0.004	0.000	0.001	0.001	**46.5**
HRM-N11	0.086	0.093	0.092	0.072	0.078	0.077	-0.014	-0.015	-0.015	**1.48**
IPS LC	0.122	0.100	0.095	0.122	0.100	0.095	0.000	0.000	0.000	**2.75**
HRM-N4	0.165	0.163	0.156	0.109	0.108	0.103	-0.056	-0.055	-0.053	**1.69**

(a)

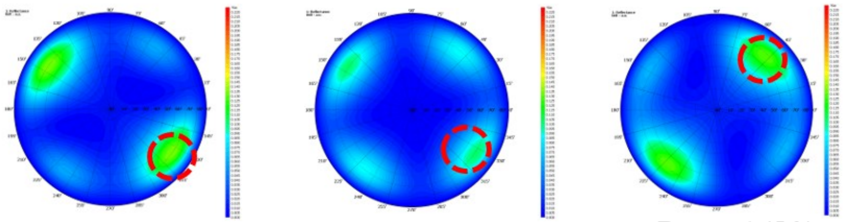


R_{center} = 7.96 %
R_{max} = 22.2 %
R_{avg} = 7.89 %

R_{center} = 0.03 %
R_{max} = 7.31 %
R_{avg} = 1.46 %

R_{center} = 3.14 %
R_{max} = 10.6 %
R_{avg} = 3.62 %

(b)

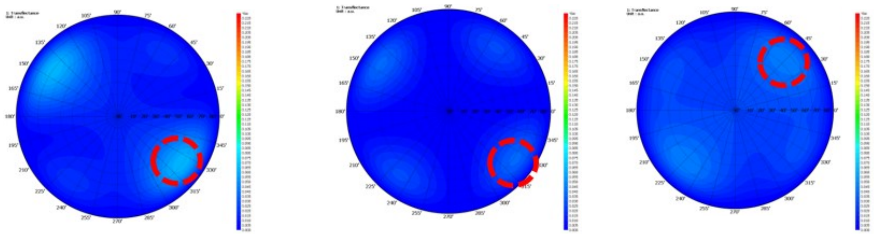


R_{center} = 0.71 %
R_{max} = 13.3 %
R_{avg} = 2.66 %

R_{center} = 0.03 %
R_{max} = 10.2 %
R_{avg} = 2.23 %

R_{center} = 1.45 %
R_{max} = 12.9 %
R_{avg} = 3.16 %

(c)



R_{center} = 1.32 %
R_{max} = 6.32 %
R_{avg} = 1.66 %

R_{center} = 0.03 %
R_{max} = 3.64 %
R_{avg} = 0.63 %

R_{center} = 2.49 %
R_{max} = 4.38 %
R_{avg} = 2.37 %

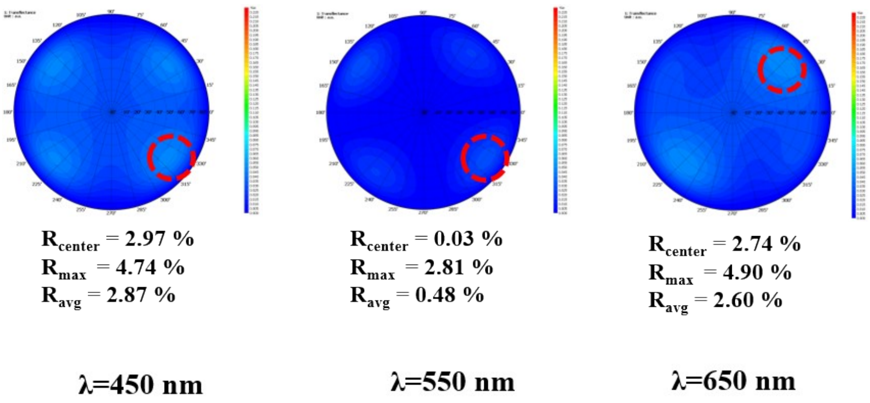
(d)

R_{center} = 1.32 %
R_{max} = 6.32 %
R_{avg} = 1.66 %

R_{center} = 0.03 %
R_{max} = 3.64 %
R_{avg} = 0.63 %

R_{center} = 2.49 %
R_{max} = 4.38 %
R_{avg} = 2.37 %

Fig. S4. Optical simulation results of the reflectance from the metal layer of the OLED display where the circular polarizer is attached. (a) Pure RRM, (b) WRS, (c) 50 wt% HRM-N11 and (d) 50 wt% HRM-N4 were used as a quarter waveplate. The red dotted circle corresponds to the viewing angle with the R_{max} value.


R_{center} = 2.97 %
R_{max} = 4.74 %
R_{avg} = 2.87 %

R_{center} = 0.03 %
R_{max} = 2.81 %
R_{avg} = 0.48 %

R_{center} = 2.74 %
R_{max} = 4.90 %
R_{avg} = 2.60 %

λ=450 nm **λ=550 nm** **λ=650 nm**

Fig. S5. Optical simulation results of the reflectance from the metal layer of the OLED display where the circular polarizer is attached. 90 wt% HRM-N6 was used as a quarter waveplate. The red dotted circle corresponds to the viewing angle with the R_{max} value. $\alpha_{90-HRM-N6}$, $\beta_{90-HRM-N6}$ and $NZ_{90\text{-HRM-N6}}$ were 0.97, 0.98 and 0.69, respectively.