

Fluorescent unsymmetrical emissive four-ring bent-core mesogens: 2D modulated phases

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Supporting Information

Synthesis

The synthesis of the designed compounds **1-n-m** (**m = 11, n = 10, 12, 13, 14, 15** and **16; m = 15, n = 11**) and **2-n-m** (**m = 11, n = 10, 12, 14** and **16; m = 12, 13** and **15, n = 11**) are presented in **Scheme 1** and the details are presented in electronic supplementary information (ESI). The chemical structures of the final compounds are confirmed by the elemental analysis and spectral techniques (¹H NMR and FTIR spectroscopy) and are presented in ESI.

[3-N-(4-n-undecyloxy-2-hydroxybenzylideneamino)phenol] **2**:

An ethanolic solution of 3-aminophenol (0.32 g, 3 mmol) was added to an ethanolic solution (20 ml) of 4-n-undecyloxy-2-hydroxybenzaldehyde (0.87 g, 3 mmol). The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 4 hours to yield the yellow colored Schiff's base. The precipitate was collected by filtration from the hot solution and recrystallized several times from absolute ethanol to give a pure yellow compound. Melting point = 117 °C, Yield = 0.34g, (82%). IR ν_{\max} in cm^{-1} : 1624 ($\nu_{\text{CH=N}}$, imine); 3387 ($\nu_{\text{O-H}}$, H-bonded); ¹H NMR (CDCl_3 , 400 MHz): δ = 13.42 (s, 1H, -OH), 13.39 (s, 1H, -OH), 8.39 (s, 1H, -CH=N), 7.61 (d, 1H, J = 8.4Hz, ArH), 7.45 (t, 1H, J = 8.0 Hz, ArH), 7.28-7.19 (2H, ArH), 6.69 (d, J = 7.8 Hz, 1H, ArH), 6.44 (s, 1H, ArH), 6.29 (s, 1H, Ar-H), 4.03 (t, 2H, J = 7.8Hz, -O-CH₂-), 1.69 (q, 2H, -O-CH₂-CH₂-), 1.33-1.26 (m, 16H, -(CH₂)₈-), 0.89 (t, 3H, J = 7.8Hz, -CH₃). Elemental analysis calculated for C₂₄H₃₃NO₃: C = 75.16%; H = 8.67%; N = 3.65% Found C = 75.12%; H = 8.64%; N = 3.62%.

[4-N-(4-n-decyloxy-2-hydroxybenzylideneamino)benzoic acid] **4-10**:

An ethanolic solution of 4-aminobenzoic acid (0.41 g, 3 mmol) was added to an ethanolic solution (20 ml) of 4-n-decyloxy-2-hydroxybenzaldehyde (0.83 g, 3 mmol). The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 4 hours to yield the yellow colored Schiff's base. The precipitate was collected by filtration from the hot solution and recrystallized several times from absolute ethanol to give a pure compound. Yield = 0.90 g,

(76%). IR ν_{\max} in cm^{-1} : 1626 ($\nu_{\text{CH=N}}$, imine); 1718 ($\nu_{\text{C=O}}$, acid), 3389 ($\nu_{\text{O-H}}$, H-bonded); ^1H NMR (CDCl_3 , 400 MHz): δ = 13.49 (s, 1H, -OH), 10.24 (s, 1H, -COOH), 8.27 (s, 1H, -CH=N-), 7.84 (d, 2H, J = 8.4 Hz, ArH), 7.33 (d, 2H, J = 8.0 Hz, ArH), 7.25 (d, 1H, J = 8.4 Hz, ArH), 6.78 (d, 1H, J = 8.4 Hz, ArH), 6.34 (s, 1H, ArH), 4.01 (t, 2H, J = 7.8 Hz, -O-CH₂-), 1.61 (q, 2H, -O-CH₂-CH₂-), 1.31-1.26 (m, 14H, -(CH₂)₇-), 0.88 (t, 3H, J = 7.8 Hz, -CH₃). Elemental analysis calculated for C₂₄H₃₁NO₄: C = 72.12 %; H = 7.79 %, Found C = 72.41 %; H = 7.83 %.

[4-(N-4'-n-decyloxy-2-hydroxybenzylideneamino)phenyl]-[3-(N-4'-n-undecyloxy-salicylidene-amino)benzoate], 1-10-11:

4-(N-4'-n-decyloxy-2-hydroxybenzylideneamino)benzoic acid (0.40 g; 1 mmol) was dissolved in dichloromethane, stirred with a teflon coated magnetic stirrer and a catalytic amount of N,N'-dimethylaminopyridine (DMAP) was added to the solution. To the stirred reaction mixture a solution 3-(N-4'-n-undecyloxy-2-hydroxybenzylideneamino)phenol (0.38 ml, 1 mmol) was slowly added. To the resulting solution an equimolar quantity of dicyclohexylcarbodiimide (DCC) (0.206 g, 1 mmol) was added and stirred for 48 hours. After the completion of stirring, the dicyclohexylurea thus formed in the reaction mixture was filtered off. Evaporation of the solvent gives the crude product which was then recrystallized several times from ethanol to obtain the pure product as yellow solid. Yield = 0.56 g, (74%).

IR ν_{\max} in cm^{-1} : 1622 ($\nu_{\text{CH=N}}$, imine); 1726 ($\nu_{\text{C=O}}$, ester), 3371 ($\nu_{\text{O-H}}$, H-bonded); ^1H NMR (CDCl_3 , 500 MHz): δ = 13.50 (s, 1H, OH), 13.37 (s, 1H, -OH), 8.57 (s, 1H, CH=N), 8.55 (s, 1H, -CH=N-), 8.23 (d, 2H, J = 8.7 Hz, ArH), 7.46 (t, 1H, J = 7.8 Hz, ArH), 7.34 (d, 2H, J = 8.4 Hz, ArH), 7.29 (d, 2H, J = 8.4 Hz, ArH), 7.10-7.18 (m, 3H, ArH), 6.47-6.52 (m, 4H, ArH), 4.00 (t, 4H, J = 6.0 Hz, -O-CH₂-), 1.82-1.74 (q, 4H, -CH₂-CH₂-), 1.59-1.09 (m, 30H, -(CH₂)₁₅-), 0.88 (t, 6H, -CH₃). Elemental analysis calculated for C₄₈H₆₂N₂O₆: C = 75.56 %; H = 8.19 %, Found C = 75.45 %; H = 8.16 %.

[3-N-(4-n-undecyloxy-2-hydroxybenzylideneamino)benzoic acid] 5:

The synthesis of [3-N-(4-n-undecyloxy-2-hydroxybenzylideneamino)benzoic acid] was carried out following the procedure adopted for **4-10** using the starting materials 4-n-undecyloxy-2-hydroxybenzaldehyde (0.87 g, 3 mmol) with 3-aminobenzoic acid (0.41 g, 3 mmol). Yield: 0.97 g (79%). IR ν_{\max} in cm^{-1} : 1617 ($\nu_{\text{CH=N}}$, imine); 1722 ($\nu_{\text{C=O}}$, acid), 3398 ($\nu_{\text{O-H}}$, H-bonded); ^1H NMR (CDCl_3 , 400 MHz): δ = 13.50 (s, 1H, -OH), 10.21 (s, 1H, -COOH), 8.32 (s, 1H, -CH=N-), 7.81 (d, 1H, J = 8.4 Hz, ArH), 7.44 (d, 2H, J = 8.4 Hz, ArH), 7.32 (t, 1H, J = 8.0 Hz, ArH), 7.25 (d, 1H, J = 7.8 Hz, ArH), 7.00 (d, 1H, J = 8.4 Hz, ArH), 6.45 (s, 1H, ArH), 4.05 (t, 2H, J = 7.8 Hz, -O-CH₂-), 1.61 (q, 2H, -O-CH₂-CH₂-), 1.31-1.22 (m, 16H, -O-(CH₂)₂-(CH₂)₈-),

0.89 (t, 3H, $J = 7.8\text{Hz}$, $-\text{CH}_3$). Elemental analysis calculated for $\text{C}_{25}\text{H}_{33}\text{NO}_4$: C = 72.96%; H = 8.08%; N = 3.40% Found C = 72.93%; H = 8.05%; N = 3.37%.

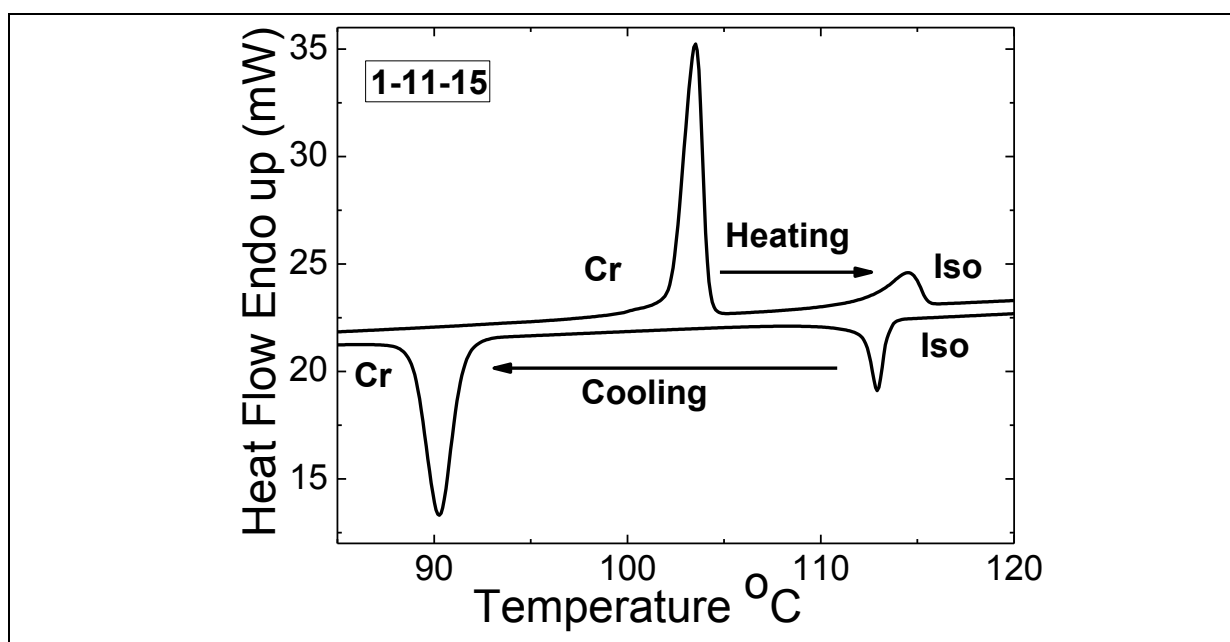
[4-N-(4-n-dodecyloxy-2-hydroxybenzylideneamino)phenol] 6-12:

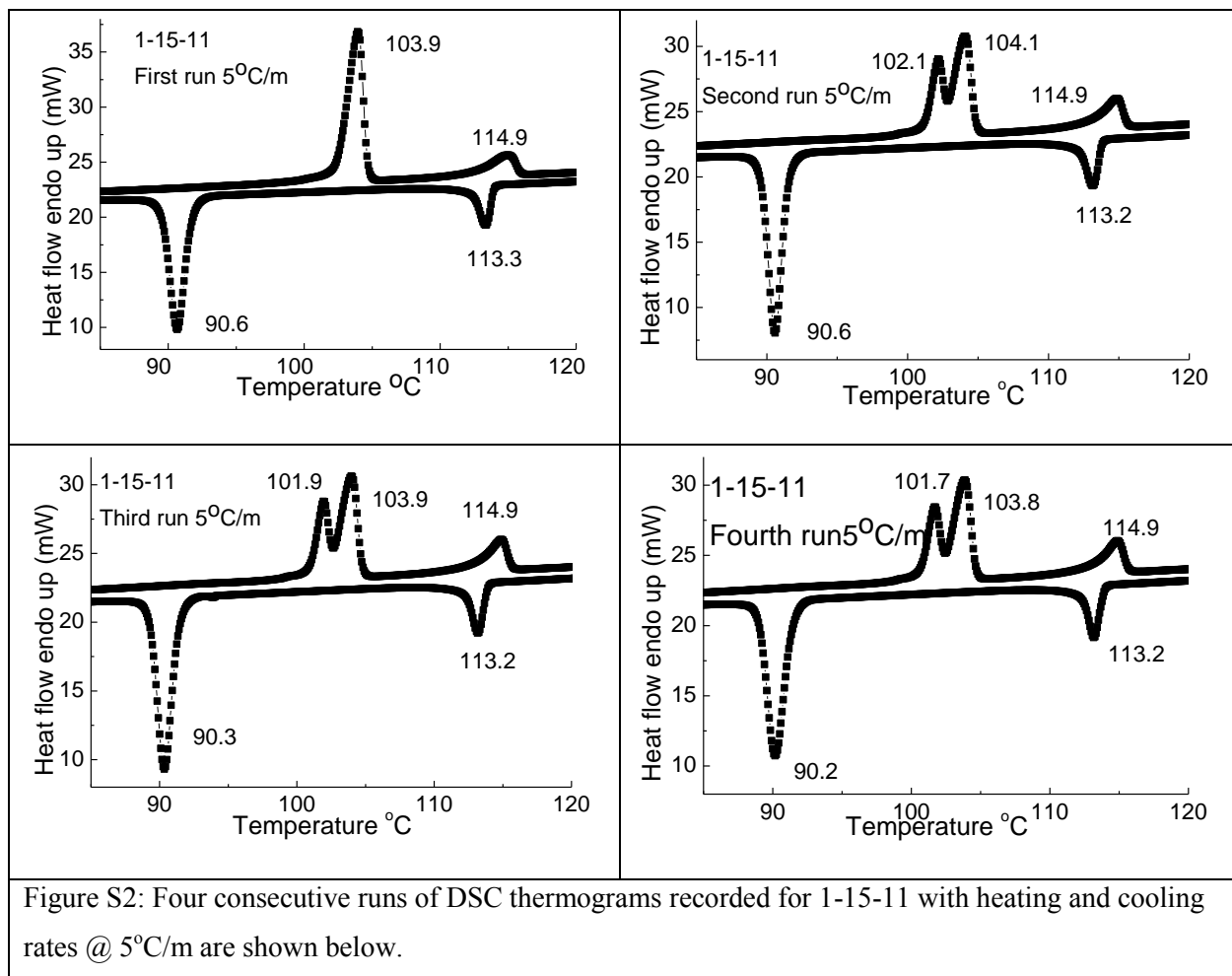
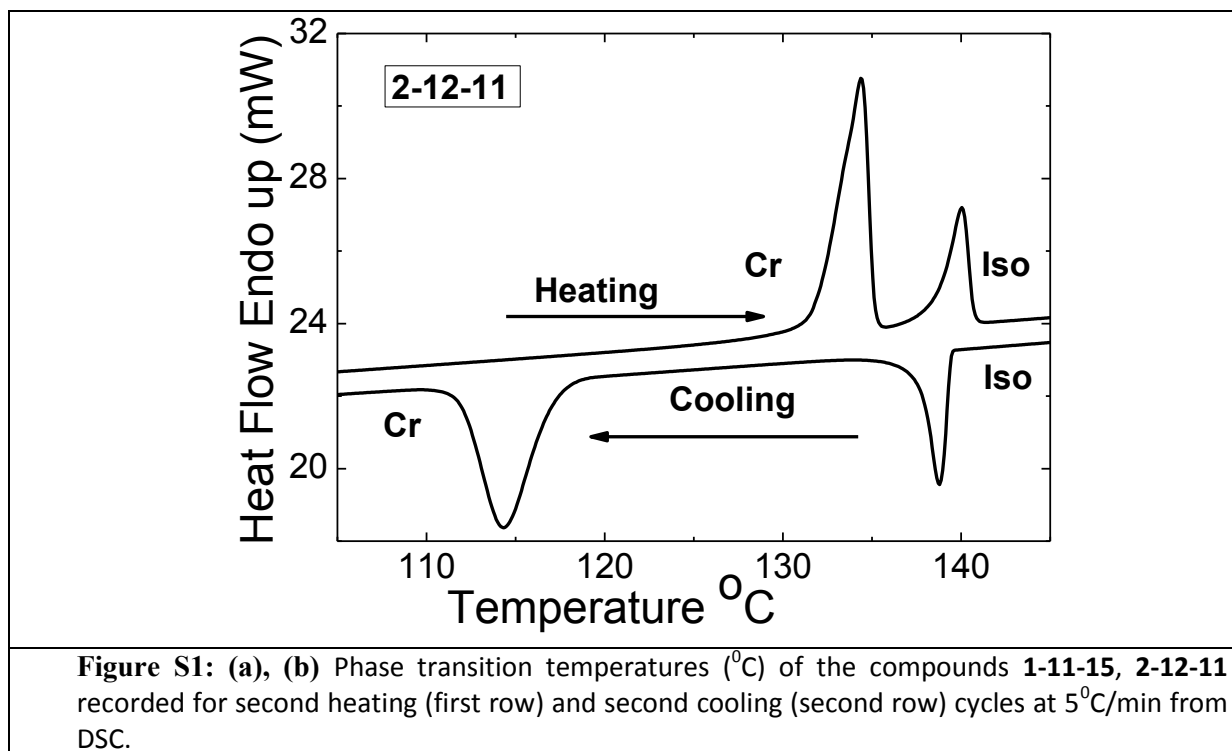
An ethanolic solution of 4-aminophenol (0.32g, 3 mmol) was added to an ethanolic solution (20 ml) of 4-n-dodecyloxy 2-hydroxybenzaldehyde (0.91 g, 3 mmol). The mixture was refluxed with a few drops of glacial acetic acid as catalyst for 4 hours to yield the yellow colored Schiff's base. The precipitate was collected by filtration from the hot solution and recrystallized several times from absolute ethanol to give a pure yellow compound. Yield = 0.97 g, (82%).

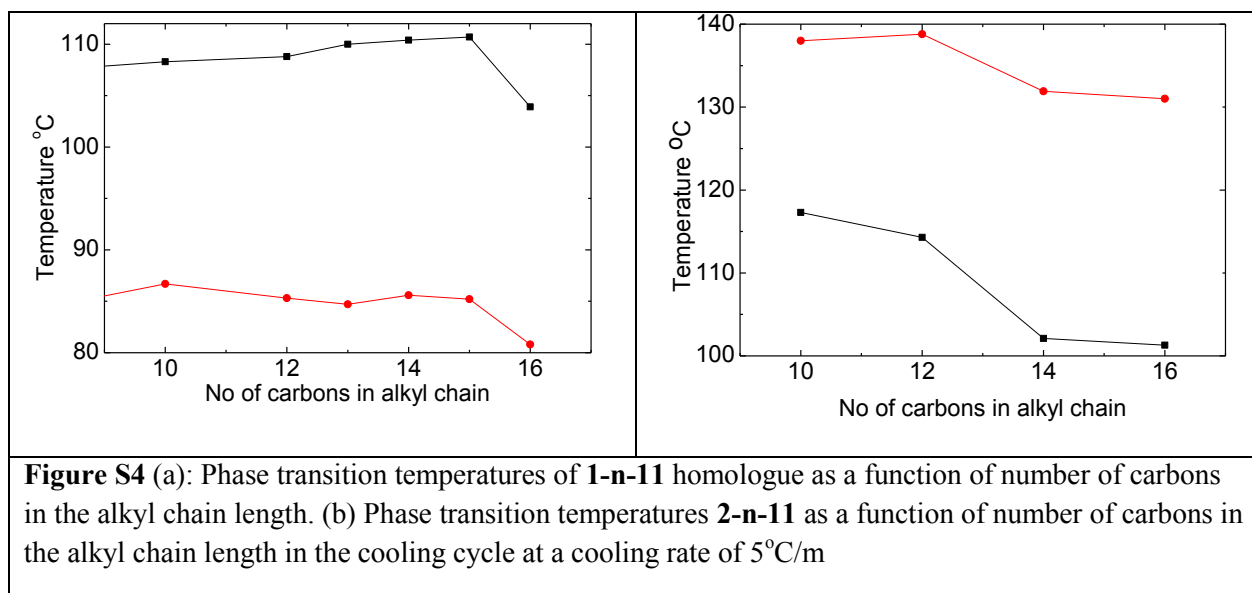
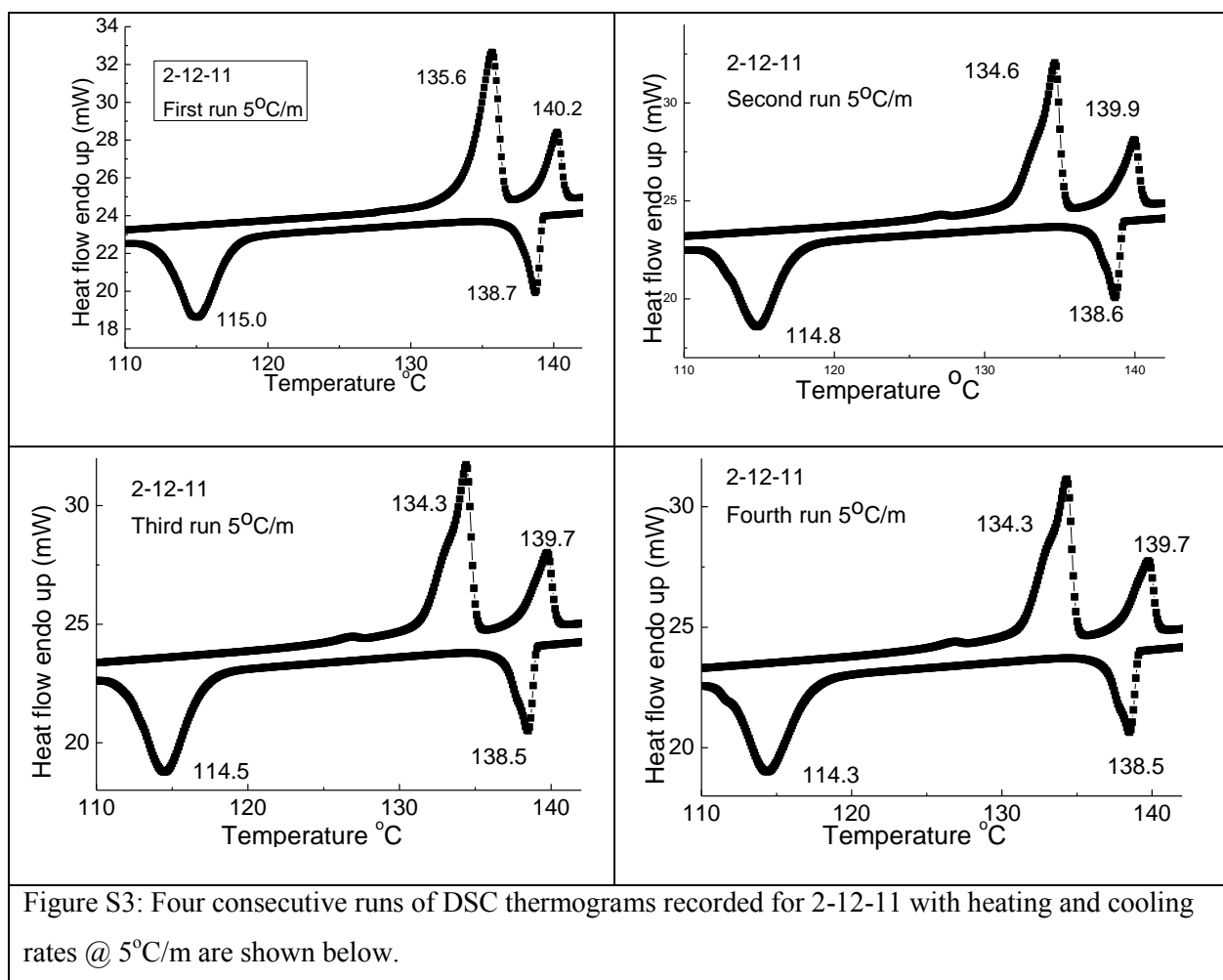
[4-(N-4'-n-dodecyloxy-2-hydroxybenzylideneamino)phenyl]-[3-(N-4'-n-undecyloxy-2-hydroxybenzylideneamino)-benzoate], 2-12-11

2-12-11 was synthesized following the procedure adopted for 1-10-11. The pure product was obtained as yellow solid. Yield = 0.57 g, (73%).

IR ν_{max} in cm^{-1} : 1624 ($\nu_{\text{CH=N}}$, imine); 1741 ($\nu_{\text{C=O}}$, ester), 3429 ($\nu_{\text{O-H}}$, H-bonded); ^1H NMR (CDCl_3 , 500 MHz): $\delta = 13.62$ (s, 1H, OH), 13.46 (s, 1H, OH), 8.61 (s, 1H, $-\text{CH=N}$), 8.54 (s, 1H, $-\text{CH=N-}$), 8.23 (d, 1H, $J = 8.7$ Hz, ArH), 8.08 (d, 1H, $J = 8.7$ Hz, ArH), 7.55 (t, 1H, $J = 7.8$ Hz, ArH), 7.32 (d, 2H, $J = 8.4$ Hz, ArH), 7.26 (d, 2H, $J = 8.4$ Hz, ArH), 7.10-7.18 (m, 3H, ArH), 6.49-6.51 (m, 4H, ArH), 4.01-3.99 (t, 4H, $J = 6.0\text{Hz}$, $-\text{O-CH}_2-$), 1.82-1.77 (q, 4H, $-\text{CH}_2-\text{CH}_2-$), 1.65-1.26 (m, 35H, $-(\text{CH}_2)_2-$), 0.88 (t, 6H, $-\text{CH}_3$). Elemental analysis calculated for $\text{C}_{50}\text{H}_{66}\text{N}_2\text{O}_6$: C = 75.91 %, H = 8.41 %, Found C = 75.58 %, H = 8.24 %.







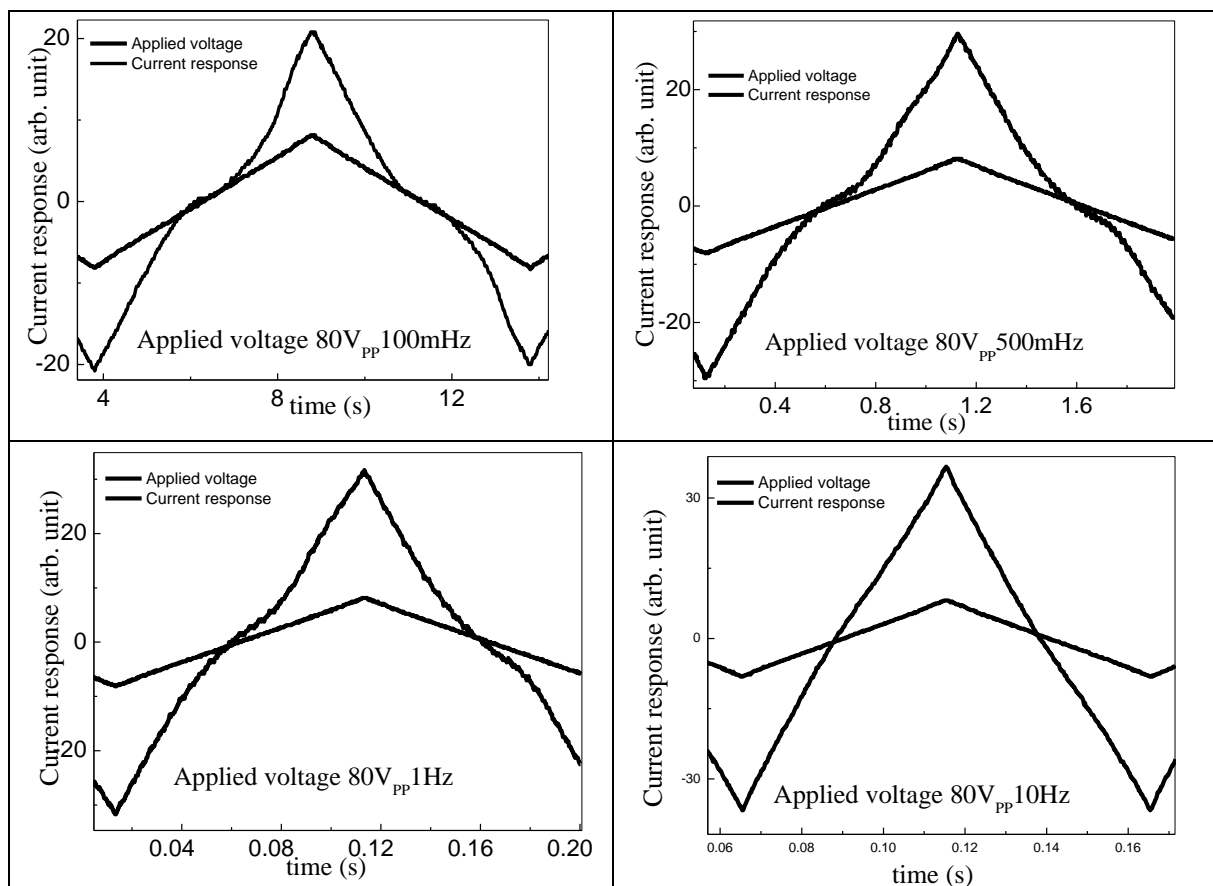


Figure S5: The switching current response obtained by applying a triangular-wave field of ± 80 V_{pp} for compound 1-15-11 at 105 °C at different frequencies.

Table S1: DFT calculated bend angle Θ as shown in Figure 7 , dipole moment components (μ_x , μ_y , μ_z), and the resultant dipole moment (μ).						
Compounds	Dipole moment (Debye)				Bend angle (degree)	Molecular length(Å)
	μ_x	μ_y	μ_z	$\mu_{\text{resultant}} = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$		
1-10-11	1.51	2.19	1.14	2.90	125	49.2
1-11-11	1.55	1.87	1.42	2.82	124	50.1
1-12-11	1.39	2.00	0.43	2.48	123	51.5
1-13-11	1.36	1.93	0.44	2.40	123	52.6
1-14-11	1.38	1.57	0.63	2.18	120	52.8
1-15-11	1.38	1.45	0.80	2.16	120	54.0
1-16-11	1.38	1.54	0.78	2.21	120	55.3
2-10-11	0.86	4.38	5.39	7.00	141	51.1
2-11-11	0.86	4.26	5.38	6.92	141	52.3
2-12-11	0.88	4.26	5.46	6.98	141	53.6
2-13-11	0.88	4.15	5.44	6.91	141	54.8
2-14-11	0.90	4.16	5.51	6.97	141	56.1
2-15-11	0.91	4.06	5.49	6.89	141	57.4
2-16-11	0.92	4.08	5.55	6.96	141	58.6

The values relative to angles and dipole moment are expressed in degree ($^\circ$) and Debye (D) respectively.

Table S2: DFT calculated principal polarizability components (α_{XX} , α_{YY} , α_{ZZ}), isotropic polarizability $\alpha^{iso} = (\alpha_{XX} + \alpha_{YY} + \alpha_{ZZ})/3$, Polarizability anisotropy $\Delta\alpha = [\alpha_{XX} - (\alpha_{YY} + \alpha_{ZZ})/2]$, and asymmetry parameter, $\eta = [(\alpha_{YY} - \alpha_{ZZ}) / (\alpha_{XX} - \alpha^{iso})]$. Parameters relative to the molecular polarizability tensor in the Cartesian reference frame

Compound	α_{XX}	α_{YY}	α_{ZZ}	α_{iso}	$\Delta\alpha$	η_α
1-10-11	1167	569	377	705	694	0.41
1-11-11	1177	579	393	716	691	0.40
1-12-11	1198	610	382	730	702	0.48
1-13-11	1216	620	391	742	711	0.48
1-14-11	1215	649	402	755	690	0.53
1-15-11	1231	654	416	767	696	0.51
1-16-11	1247	666	425	779	702	0.51
2-10-11	1203	463	434	700	755	0.05
2-11-11	1221	471	445	712	763	0.05
2-12-11	1239	480	455	725	772	0.05
2-13-11	1257	488	466	737	780	0.04
2-14-11	1275	498	476	749	788	0.04
2-15-11	1291	506	487	762	795	0.03
2-16-11	1310	516	497	774	804	0.03

All polarizability components and the anisotropy parameter are calculated in Bohr³ (with 1 Bohr = 0.52917 Å).